REGISTERED NO. M. 3121

PROCEEDINGS

OF THE

INDIAN ACADEMY

OF SCIENCES

VOL. XIII] *SECTION A* [NO. 6

JUNE, 1941

Price Rs. 2 or 3 Sh. *Annual Subscription Rs. 18*

PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY G. SRINIVASA RAO,
SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF SCIENCES,
BANGALORE.

THE SPECTRAL CHARACTER OF THE REFLECTION BY A REGULARLY STRATIFIED MEDIUM: PART I

By R. V. Subrahmanian

(*From the Department of Physics, Indian Institute of Science, Bangalore*)

Received May 1, 1941

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. *Introduction*

It is well known that a regularly stratified medium is capable under suitable conditions of giving a powerful monochromatic reflection of the light incident on it. Numerous examples of such stratified media, both natural and artificial and the effects exhibited by them are familiar to students of optics. Mother-of-pearl, precious opal, iridiscent crystals of potassium chlorate and metallically coloured beetles may be mentioned in this connection. Amongst artificially produced structures, the well-known Lippman photographic films and the iridiscent colloidal precipitates discovered by Zocher may be referred to. The optical theory of stratified media was developed by the late Lord Rayleigh (1917) on a consideration of the multiple reflections which occur at the sharply defined boundaries between parallel plates of alternating thickness and refractive index. It is proposed in the present paper to treat the same problem by the standard methods of the electromagnetic theory of light. The formulæ deduced are naturally the same as those obtained by Rayleigh, but their detailed discussion is carried much further than was undertaken by him. In particular, the spectral character of the reflected light is computed and discussed for a variety of cases.

2. *The Case of a Single Plate*

Here we follow the same method as that adopted by Drude. Consider a plane parallel plate of transparent material of thickness d placed in the path of a parallel beam of light. The dielectric coefficient of the material of the plate is ϵ_2, that of the surrounding medium ϵ_1. As usual X_e, Y_e and Z_e refer to the x, y and z components of the electric force in the incident wave, α_e, β_e and γ_e to the components of the magnetic force, the same symbols with the subscripts r and t referring to the corresponding quantities in the reflected and transmitted waves.

The first surface of the plate upon which the light is incident is denoted the xy plane, the second surface $Z = d$. For simplicity the incidence is

assumed to be normal and the incident light to satisfy the conditions,

$$X_e = O,\ Y_e = Ee^{i\frac{2\pi}{\tau}(t - z/v_1)},\ Z_e = O \tag{1}$$

The condition $X_e = O$, does in no way mar the generality of the conclusions, since at normal incidence all results which hold for the y component hold without change for the x component also. If (1) represents the incident electric vector, the magnetic vector is represented by

$$\alpha_e = -E\sqrt{\epsilon_1}\, e^{i\frac{2\pi}{\tau}(t - z/v_1)},\ \beta_e = O \text{ and } \gamma_e = O. \tag{2}$$

The reflected wave is given by

$$X_r = O,\ Y_r = R\, e^{i\frac{2\pi}{\tau}(t + z/v_1)},\ Z_r = O$$

$$\alpha_r = R\sqrt{\epsilon_1}\, e^{i\frac{2\pi}{\tau}(t + z/v_1)},\ \beta_r = O,\ \gamma_r = O.$$

The repeated reflections and refractions taking place at the surfaces of the plate can be taken account of in a simple way by considering the net effect of these to be replaced by two waves, propagated within the plate, one along the + ve and the other along the − ve direction of the Z axis. For the former the following equations hold

$$X' = O,\ Y' = D_1'\, e^{i\frac{2\pi}{\tau}(t - z/v_2)},\ Z' = O,$$

$$\alpha' = -D_1'\sqrt{\epsilon_2}\, e^{i\frac{2\pi}{\tau}(t - z/v_2)},\ \beta' = O,\ \gamma' = O,$$

while for the latter

$$X'' = O,\ Y'' = D_1''\, e^{i\frac{2\pi}{\tau}(t + z/v_2)},\ Z'' = O.$$

$$\alpha'' = D_1''\sqrt{\epsilon_2}\, e^{i\frac{2\pi}{\tau}(t + z/v_2)},\ \beta'' = O,\ \gamma'' = O.$$

Finally for the emergent wave,

$$X_t = O,\ Y_t = D_2'\, e^{i\frac{2\pi}{\tau}(t - z/v_1)},\ Z_t = O,$$

$$\alpha_t = -D_2'\sqrt{\epsilon_1}\, e^{i\frac{2\pi}{\tau}(t - z/v_1)},\ \beta_t = O,\ \gamma_t = O.$$

Applying the boundary conditions at both the surfaces, we have

$$\left.\begin{aligned} Y_e + Y_r &= Y' + Y'' \\ \alpha_e + \alpha_r &= \alpha' + \alpha'' \end{aligned}\right\} \text{for } Z = O.$$

and

$$\left.\begin{aligned} Y' + Y'' &= Y_t \\ \alpha' + \alpha'' &= \alpha_t \end{aligned}\right\} \text{for } Z = d.$$

These conditions give

$$E + R = D_1' + D_1''$$
$$(E - R)\sqrt{\epsilon_1} = (D_1' - D_1'')\sqrt{\epsilon_2}$$
$$D_1' e^{-ip} + D_1'' e^{ip} = D_2' e^{-iq}$$
$$(D_1' e^{-ip} - D_1'' e^{ip})\sqrt{\epsilon_2} = D_2' e^{-iq}\sqrt{\epsilon_1},$$

where $p = \frac{2\pi d}{\tau \cdot v_2}$, $q = \frac{2\pi d}{\tau \cdot v_1}$.

From these equations it is easily deduced

$$\frac{R}{E} = r = \eta \frac{(1 - e^{2ip})}{e^{2ip} - \eta^2} \text{ where } \eta = \frac{\sqrt{\epsilon_2} - 1}{\sqrt{\epsilon_1}} \Big/ \frac{\sqrt{\epsilon_2/\epsilon_1} + 1}{\sqrt{\epsilon_1}}$$

which on rationalising leads to the familiar expression

$$r = \frac{\eta (1 + \eta^2)(\cos 2p - 1)}{1 + \eta^4 - 2\eta^2 \cos 2p}$$

where $\sqrt{\epsilon_2/\epsilon_1} = \mu$ the refractive index of the material of the plate with respect to the surrounding medium, and $\eta^2 =$ reflecting power.

Again $\frac{D_1' e^{-iq}}{E} = t = \frac{(1 - \eta^2) e^{ip}}{e^{2ip} - \eta^2}$, r and t denoting respectively the amplitudes of the reflected and transmitted vibrations. It is clear $|r^2| + |t^2| = 1$, as is to be expected when there is no absorption. Further $r/t = \frac{\eta (1 - e^{2ip})}{1 - \eta^2} e^{-ip}$ a complex quantity, so that it is justifiable to write

$$\left.\begin{aligned} r &= \sin\theta\, e^{i\rho} \\ t &= i \cos\theta\, e^{i\rho} \end{aligned}\right\}$$

3. *The General Case of* $(m + n)$ *Plates*

Next we pass on to consider the operation of a number of plates of equal thickness d, separated by equal intervals d_1. Here again the infinite number of reflected and refracted rays at each surface are replaced by the equivalent concept of two waves travelling in opposite directions, everywhere within the periodic structure. When the total number of plates is small say only two or three, the solution is not difficult and by the same method as that applied in the case of a single plate, we get the amplitude of the wave reflected from two plates

$$\phi_2 = \frac{\eta [e^{2is}(e^{2ip} - \eta^2) + (1 - e^{2ip})] - \eta e^{2ip} [(e^{2ip} - \eta^2) e^{2is} + \eta^2 (1 - e^{2ip})]}{e^{2ip} [(e^{2ip} - \eta^2) e^{2is} + \eta^2 (1 - e^{2ip})] - \eta^2 [e^{2is}(e^{2ip} - \eta^2) + (1 - e^{2ip})]}$$

where $s = \frac{2\pi}{\lambda_1} d_1$, $r = \frac{2\pi}{\lambda_2} d_1$. Similarly ϕ_3 can be evaluated.

When there are in general $(m+n)$ plates the resulting equations on applying the boundary conditions at each surface are,

$$E+R=D_1'+D_1''$$

$$E-R=(D_1'-D_1'')\mu$$

$$D_1'\,e^{-i\beta}+D_1''\,e^{i\beta}=D_2'\,e^{-iq}+D_2''\,e^{iq}$$

$$(D_1'\,e^{-i\beta}-D_1''\,e^{i\beta})\mu=D_2'\,e^{-iq}-D_2''\,e^{iq}$$

. . . . . .

. . . . . .

$$D'_{2n+1}\,e^{-i(\overline{n+1}\,\beta+nr)}+D''_{2n+1}\,e^{i(\overline{n+1}\,\beta+nr)}=D'_{2n+2}\,e^{-i(\overline{n+1}\,q+ns)}+D''_{2n+2}\,e^{i(\overline{n+1}\,q+ns)}$$

$$\mu\{D'_{2n+1}\,e^{-i(\overline{n+1}\,\beta+nr)}-D''_{2n+1}\,e^{i(\overline{n+1}\,\beta+nr}\}=D'_{2n+2}\,e^{-i(\overline{n+1}\,q+ns)}-D''_{2n+2}\,e^{i(\overline{n+1}\,q+ns)}$$

. . . . . .

. . . . . .

$$D'_{2(m+n)-1}\,e^{-i(\overline{m+n}\,\beta+\overline{m+n-1}\,r)}+D''_{2(m+n)-1}\,e^{i(\overline{m+n}\,\beta+\overline{m+n-1}\,r)}=D'_{2(m+n)}\,e^{-i(\overline{m+n}\,q+\overline{m+n-1}\,s)}$$

$$\mu\{D'_{2(m+n)-1}\,e^{-i(\overline{m+n}\,\beta+\overline{m+n-1}\,r)}-D''_{2(m+n)-1}\,e^{i(\overline{m+n}\,\beta+\overline{m+n-1}\,r)}\}=D'_{2(m+n)}\,e^{-i(\overline{m+n}\,q+\overline{m+n-1}\,s)}$$

From the above equations, by successive elimination,

$$\frac{D''_{2(m+n-1)}}{D'_{2(m+n-1)}}=\phi_1\,e^{-2i(m+n-1)(q+s)}$$

and

$$\frac{D''_{2(m+n-2)}}{D'_{2(m+n-2)}}=\phi_2\,e^{-2i(m+n-2)(q+s)}$$

so that

$$\frac{D''_{2n}}{D'_{2n}}=\phi_m\,e^{-2in(q+s)}.$$

Further expressing D'_{2n+3} in terms of D'_{2n+2}, D''_{2n+2}, D'_{2n+4} and D''_{2n+4}, we have

$$2\,D'_{2n+3}\,e^{-i(\overline{n+2}\,\beta+\overline{n+1}\,r)}=D'_{2n+1}\,e^{-i(\overline{n+2}\,q+\overline{n+1}\,s)}\left(1+\frac{1}{\mu}\right)+D''_{2n+4}\,e^{i(\overline{n+2}\,q+\overline{n+1}\,s)}\left(1-\frac{1}{\mu}\right)\qquad(a)$$

Also

$$2\,D'_{2n+3}\,e^{-i(n+1)(p+r)} = D'_{2n+2}\,e^{-i(n+1)(q+s)}\left(1+\frac{1}{\mu}\right) + D''_{2n+2}\,e^{i(n+1)(q+s)}\left(1-\frac{1}{\mu}\right) \qquad (b)$$

From (a) and (b)

$$\frac{D'_{2n+2}\,e^{-i(n+1)(q+s)}(\mu+1)+D''_{2n+2}\,e^{i(n+1)(q+s)}(\mu-1)}{D'_{2n+4}\,e^{-i(n+2q+n+1s)}(\mu+1)+D''_{2n+4}\,e^{i(n+2q+n+1s}(\mu-1)} = e^{ip} \qquad (c)$$

Similarly expressing D''_{2n+3} in terms of the same quantities, and finally eliminating it

$$\frac{D'_{2n+2}\,e^{-i(n+1)(q+s)}(\mu-1)+D''_{2n+2}\,e^{i(n+1)(q+s)}(\mu+1)}{D'_{2n+4}\,e^{-i(n+2q+n+1s)}(\mu-1)+D''_{2n+4}\,e^{i(n+2q+n+1s)}(\mu+1)} = e^{-ip} \qquad (d)$$

Dividing (c) by (d), and remembering,

$\frac{D''_{2n}}{D'_{2n}} = \phi_m\,e^{-2in(q+s)}$, we have

$$\frac{(1+\eta\,\phi_{m-(n+1)})}{(1+\eta\,\phi_{m-(n+2)}\,e^{-2is})}\cdot\frac{\eta+\phi_{m-(n+2)}\,e^{-2is}}{\eta+\phi_{m-(n+1)}} = e^{2ip}.$$

This equation is true for all values of m and n. Putting $n+1=0$, we have

$$\frac{1+\eta\,\phi_m}{1+\eta\,\phi_{m-1}e^{-2is}}\cdot\frac{\eta+\phi_{m-1}e^{-2is}}{\eta+\phi_m} = e^{2ip}.$$

Whence

$$\phi_m = \frac{(1-\eta^2)(\eta+\phi_{m-2}e^{-2is})-\eta\,e^{2ip}(1+\eta\,\phi_{m-1}e^{-2is})+\eta^2(\eta+\phi_{m-1}e^{-2is})}{e^{2ip}(1+\eta\,\phi_{m-1}e^{-2is})-\eta(\eta+\phi_{m-1}e^{-2is})}$$

$$\phi_m = r + \frac{t^2\phi_{m-1}e^{-2is}}{1-r\,\phi_{m-1}e^{-2is}}, \text{ since}$$

$$r = \frac{\eta(1-e^{2ip})}{e^{2ip}-\eta^2} \text{ and } t = \frac{(1-\eta^2)\,e^{ip}}{e^{2ip}-\eta^2}.$$

Thus we arrive at the same expression as that first obtained by Stokes and later on independently by Rayleigh.

4. *Evaluation of the Intensity*

$\phi_{m+1} = r + \dfrac{t^2 \phi_m e^{-2is}}{1 - r\phi_m e^{-2is}}$. Following the method of Rayleigh, we write, $r\phi_m e^{-2is} - 1 = \dfrac{V_{m+1}}{V_m}$ and with this substitution,

$$V_{m+2} + (1 - r^2 - t^2 e^{-2is}) V_{m+1} + t^2 e^{-2is} V_m = O.$$

This is a standard type of functional equation the solution of which is given by $V_m = H P^m + K Q^m$,

H and K being arbitrary constants.

$P + Q = (r^2 - t^2) e^{-2is} - 1$, $PQ = t^2 e^{-2is}$. To find H and K,

$$\frac{V_2}{V_1} = r^2 e^{-2is} - 1 = \frac{H P^2 + K Q^2}{H P + K Q}.$$

and further $(P+1)(Q+1) = r^2 e^{-2is}$, so that

$$(P+1) H + (Q+1) K = O.$$

It follows then that

$$\phi_m = \frac{(P+1)(Q+1)\{P^m - Q^m\}}{r\{(Q+1) P^m - (P+1) Q^m\}} e^{2is}$$

and since $(P+1)(Q+1) = r^2 e^{-2is}$

$$\phi_m = \frac{b^m - b^{-m}}{ab^m - a^{-1} b^{-m}} \text{ where } a = \sqrt{\frac{Q+1}{P+1}},\ b = \sqrt{\frac{P}{Q}}$$

$$= \frac{\sinh m\beta}{\sinh(\alpha + m\beta)},$$

if we write $b = e^{\beta}$, and $a = e^{\alpha}$.

when $m = 1$, $\phi_1 = \dfrac{\sinh \beta}{\sinh(\alpha+\beta)} = r$

and consequently $t = \dfrac{\sinh \alpha}{\sinh(\alpha+\beta)}$.

From the above relations it is readily seen that, $\cosh \alpha = \dfrac{1 + r^2 - t^2}{2r} = \dfrac{\cos \rho}{\sin \theta}$. Substituting for r and t in terms of p, s and η, $\sinh^2 \alpha = \{\cos^2 \tfrac{1}{2}(p+s) - \eta^2 \cos^2 \tfrac{1}{2}(p-s)\} \dfrac{\{\sin^2 \tfrac{1}{2}(p+s) - \eta^2 \sin^2 \tfrac{1}{2}(p-s)\}}{\eta^2 \sin^2 p}$. This relation gives the value of α, when p, s & η are known.

But $r = \dfrac{\sinh \beta}{\sinh(\alpha+\beta)}$, $\dfrac{1}{|r|^2} = 1 + \dfrac{(1-\eta^2)^2}{2\eta^2(1 - \cos 2p)}$. α is known. Hence β can be calculated from the above equation.

Thus $|\phi_m|^2 = \dfrac{\sinh^2 m\beta}{\sinh^2(\alpha + m\beta)}$ gets evaluated.

Now, $\cosh \alpha = \dfrac{1 + r^2 - t^2}{2r} = \dfrac{\cos\rho}{\sin\theta}$, a real quantity.

$\therefore \sinh^2 \alpha = \dfrac{\cos^2\rho}{\sin^2\theta} - 1$, so that α is complex and can be written $= \alpha_1 + i\alpha_2$. Similarly $\beta = \beta_1 + i\beta_2$.

$\text{Sinh } \alpha = \sinh\alpha_1 \cos\alpha_2 + i \cosh\alpha_1 \sin\alpha_2$.

Since $\cosh \alpha$ is real either $\alpha_1 = 0$ or $\sin\alpha_2 = 0$. In the first case $\sinh\alpha = i \sin\alpha_2$, and this can happen only when $\cos^2\rho < \sin^2\theta$. In the second case $\sinh^2\alpha = \sinh^2\alpha_1$, so that $\cos^2\rho > \sin^2\theta$.

Since $\cosh\beta$ is also real, arguing as before, the two alternatives are

(1) $\text{Sinh}^2\alpha = -\text{ve}$, $\sin^2\theta > \cos^2\rho$, $\alpha_1 = 0$, $\sin\beta_2 = 0$.

(2) $\text{Sinh}^2\alpha = +\text{ve}$, $\sin^2\theta < \cos^2\rho$, $\beta_1 = 0$, $\sin\alpha_2 = 0$.

In case (1) $\dfrac{1}{|\phi_m|^2} = 1 + \dfrac{\sin^2\alpha_2}{\sinh^2 m\beta_1}$. As β_1 is finite, $\sinh^2 m\beta_1 \to \infty$ as m increases indefinitely, so that the reflection tends to become complete.

In case (2) $\dfrac{1}{|\phi_m|^2} = 1 + \dfrac{\sinh^2\alpha_1}{\sin^2 m\beta_2}$, so that $|\phi_m|^2$ tends to fluctuate as m increases. The intensity of the reflected light, therefore passes through a series of maxima and minima.

5. *Influence of the Relative Thickness of the Strata*

Some limited cases of optical interest have been dealt with by Rayleigh. Representing $2\mu_2 d = \delta$, and $2\mu_1 d_1 = \delta'$, he has shown that with glass and air, for such a value of δ as would give maximum reflection from a single plate, *viz.*, $\cos k\delta = -1$, when the reflected vibrations from successive plates agree in phase, even a very small number of plates 4 or 5, leads to complete reflection. Here $k = \dfrac{2\pi}{\lambda}$ and $\eta = \dfrac{\mu - 1}{\mu + 1} = 1/5$.

He has further shown that, provided 'η' has a very small value, as in the case of potassium chlorate crystals with periodic twinning, a very large number (about 80) plates are necessary for complete reflection.

We shall choose for our illustration the familiar example of mother-of-pearl, a naturally occurring stratified medium. Mother-of-pearl consists chiefly of calcium carbonate, existing in the optically biaxial form of aragonite, together with varying amounts of an organic substance conchin, which serves

to hold the substance together. The laminations are made up of successive layers of aragonite, held together by the cementing material, there being a large number of layers running approximately parallel to the natural surface of the shell. When light is incident normally, the effective refractive index of the material of the plates is about 1·68, and that of conchin 1·53. Let us now proceed to investigate how the relative thicknesses of the alternate strata affect the reflection from the medium, when the reflections from the successive plates re-inforce each other.

$$\text{Thus } \delta + \delta' = n\lambda, \text{ and } \frac{1}{|r|^2} = 1 - \frac{\sinh^2 \alpha_1}{\sinh^2 \beta}$$

$$= 1 + \frac{(1-\eta^2)^2}{2\eta^2(1-\cos 2p)}.$$

Choosing the characteristic wave-length for third order reflection, *i.e.*, $\lambda =$ 5500 A.U., let the thickness of the aragonite plate in the first instance be $d = \cdot 45\,\mu$, and that of the conchin layer $d_1 = \cdot 05\,\mu$, *i.e.*, approximately $\frac{1}{10}$th that of the aragonite. Table I shows how the intensity of the reflected light varies with the increase in the number of plates. About 40 plates suffice to give total reflection.

TABLE I

$d = \cdot 45\,\mu$ $\qquad$ $d_1 = \cdot 05\,\mu$

No. of plates m	Intensity $\lvert \phi_m \rvert^2$
1	0·0051
5	0·1170
10	0·3750
15	0·6228
20	0·7934
25	0·8928
30	0·9453
35	0·9731
40	0·9867

In Table II, the variation of the intensity of the reflected light for different number of laminæ are given, the relative thickness of the conchin layer to the aragonite layer being about $\frac{1}{100}$. From a comparative study of the two tables it is clear, that the smaller the relative thickness of one layer

TABLE II

$d = \cdot 49\,\mu$ $\qquad$ $d_1 = \cdot 0062\,\mu$

m	$\lvert\phi_m\rvert^2$
1	0·000125
10	0·01233
20	0·0484
50	0·2573
100	0·6825
150	0·8696
200	0·9554
250	0·9823

with respect to the other, the larger the number of plates required for complete reflection. In the latter case more than 200 plates are necessary for a fairly complete reflection. This conclusion from theory is readily understood as when the thickness of one of the layers vanishes, there can be no reflection at all, even if an infinite number of plates are present.

6. *Spectral Character of the Reflected Light*

(*a*) *Influence of the number of plates.*—It now remains to investigate the distribution of energy in the spectrum of the reflected light. From the formula,

$$\sinh^2\alpha = \{\cos^2\tfrac{1}{2}(p+s) - \eta^2\cos^2\tfrac{1}{2}(p-s)\}\,\frac{\{\sin^2\tfrac{1}{2}(p+s) - \eta^2\sin^2\tfrac{1}{2}(p-s)\}}{\eta^2\sin^2 p}$$

for any value of λ, the corresponding value of $\sinh^2\alpha$ can be computed. When $\sinh^2\alpha$ is known, as in the previous cases, the calculation of the intensity of the reflected light becomes easy using the relations

$$\lvert\phi_m\rvert^2 = \frac{\sinh^2 m\beta}{\sinh^2(\alpha + m\beta)}$$

and

$$\lvert r\rvert^2 = \frac{\sinh^2\beta}{\sinh^2(\alpha+\beta)}.$$

Thus for a definite number of plates and for given thicknesses of the aragonite and conchin layers, the intensity of the reflected light for various wave-lengths are known. Table III shows the calculated values of the intensity for 100, 50, 20 and 10 plates respectively for a range of wave-lengths extending from 5200 A.U. to 6200 A.U., the thickness of the aragonite and conchin layers being assumed to be $\cdot 45\,\mu$ and $\cdot 05\,\mu$ respectively. With

TABLE III

$d = \cdot 45\,\mu$ $\qquad$ $d_1 = \cdot 05\,\mu$

λ	$\lvert\phi_m\rvert^2$ when $m=100$	$\lvert\phi_m\rvert^2$, $m=50$	$\lvert\phi_m\rvert^2$, $m=20$	$\lvert\phi_m\rvert^2$, $m=10$	λ	$\lvert\phi_m\rvert^2$, $m=100$	$\lvert\phi_m\rvert^2$, $m=50$	$\lvert\phi_m\rvert^2$, $m=20$	$\lvert\phi_m\rvert^2$, $m=10$
5250	0·0000	0·0046	0·0042	0·0029	5600	0·6884	0·7364	0·6471	0·3522
5275	0·0062	0·0025	0·0008	0·0063	5625	0·0511	0·3859	0·3578	0·3047
5300	0·0010	0·0002	0·0026	0·0086	5650	0·2073	0·1695	0·0168	0·2284
5325	0·0100	0·009	0·0134	0·0074	5675	0·0629	0·0184	0·0768	0·1325
5350	0·0009	0·0154	0·0085	0·0022	5700	0·1127	0·0588	0·1127	0·0595
5400	0·0036	0·0093	0·0232	0·0150	5725	0·0109	0·0838	0·0376	0·0109
5425	0·0226	0·0566	0·0314	0·0545	5750	0·0150	0·004	0·0006	0·0000
5450	0·0402	0·1207	0·0487	0·1255	5775	0·0530	0·0391	0·0355	0·0110
5475	0·2492	0·2123	0·1753	0·2854	5800	0·0409	0·0360	0·0494	0·0277
5500	0·5089	0·3218	0·5421	0·3156	5825	0·0000	0·0000	0·0152	0·0384
5510	0·9942	0·9417	0·6586	0·3351	5850	0·0054	0·0363	0·0002	0·0372
5520	0·9980	0·9813	0·7079	0·3529	5875	0·0273	0·0097	0·0192	0·0277
5530	0·9990	0·9922	0·7977	0·3688	5900	0·0296	0·0136	0·0299	0·0148
5540	0·9996	0·9990	0·7980	0·3820	5925	0·0202	0·0250	0·0122	0·0035
5550	1·0000	1·000	0·7994	0·3815	5950	0·0007	0·0001	0·0000	0·000
5560	0·9990	0·999	0·7987	0·3800	5975	0·0032	0·0214	0·0096	0·0027
5570	0·9990	0·9962	0·7805	0·3795	6000	0·0133	0·003	0·0203	0·009
5580	0·9988	0·9880	0·7598	0·3761	6025	0·0189	0·009	0·0124	0·015
5590	0·9960	0·9658	0·7168	0·3667					

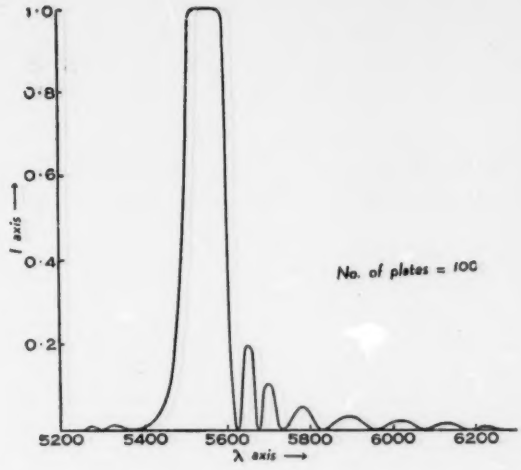


FIG. 1

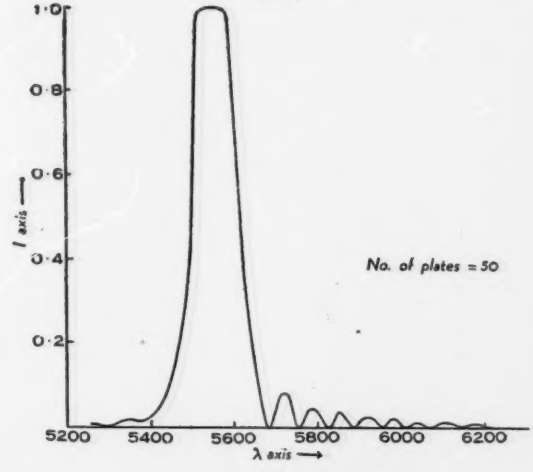


FIG. 2

the data obtained, the distribution of intensity corresponding to different wave-lenths is plotted, with wave-length as abcissæ. The curves so obtained and shown in Figs. 1, 2, 3, and 4 exhibit a remarkable asymmetry with reference to the principal band of reflection. When the number of plates is fairly large say 50 or 100, the primary band consisting of the wave-lengths selectively reflected, is sharply defined and has a width of about 100 A.U. Its intensity is very nearly unity. The primary band is accompanied on the

longer wave-length side by several secondary bands of fairly visible intensity. The shorter wave-length side presents a conspicuous contrast. Here the oscillations are few and much less marked.*

When the number of plates is about 20, the general intensity of the band gets lowered, but the sharpness remains practically unaffected. There are a number of oscillations of appreciable intensity on the longer wave-length side, the shorter wave-length side having practically none.

With a still further reduction in the number of plates the effect seems to undergo a great change. The band now begins to broaden out, so that

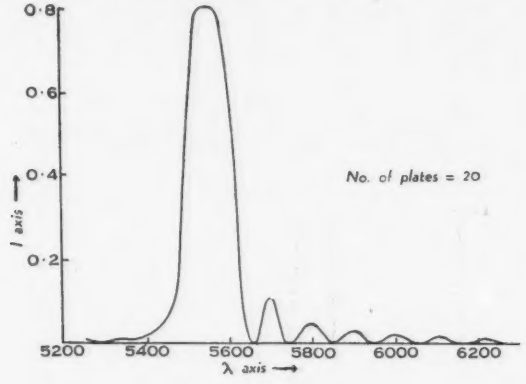


FIG. 3

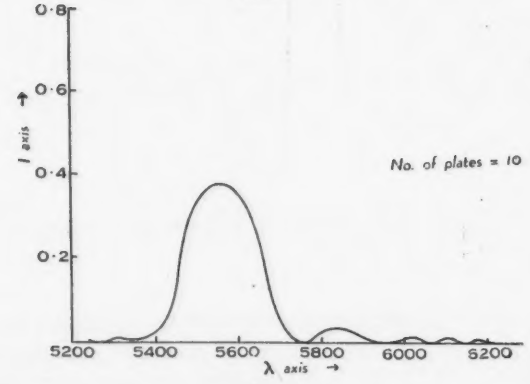


FIG. 4

* The photographs of H. E. Ives with a Lippman film, which have been reproduced by R. W. Wood in his *Physical Optics* (3rd Edition, p. 216), show an asymmetry in the distribution of the bands, these being confined to the longer wave-length side. It appears probable that this asymmetry arises in the manner explained theoretically in this paper.

when the number of plates is 10, the width of the band exceeds 300 A.U. The general intensity of the band undergoes an appreciable diminution, and the spectrum of the reflected light would appear more hazy. It appears as though the band begins to broaden, when the number of plates is less than a certain limit. The asymmetry in the distribution of the secondary bands, however persists.

(*b*) *Influence of the relative refractive index.*—Finally it will be of interest to see how the spectral distribution of intensity depends on the reflecting power. This dependence is well brought out by a study of two different stratified media, one supposed to be made up of laminations of glass intercepted by air, and the other in which air is replaced by water, the relative thicknesses of the strata being the same in both. The intensity distribution curves are drawn for both. It is readily seen that when the strata are alternately made up of glass and air, the general intensity of the reflected light for a given number of plates is more than what it would be for glass and water. This can be accounted for as being due to the higher reflecting power of the former medium. But the bands are more sharply defined for the latter, with the result that the colours observed with reflected light should be more vivid than in the other case. It might also be mentioned that for higher values of reflecting power, there appear some oscillations on the shorter wave-length side also. These results are shown in Table IV and are illustrated in Figs. 5, 6, 7 and 8.

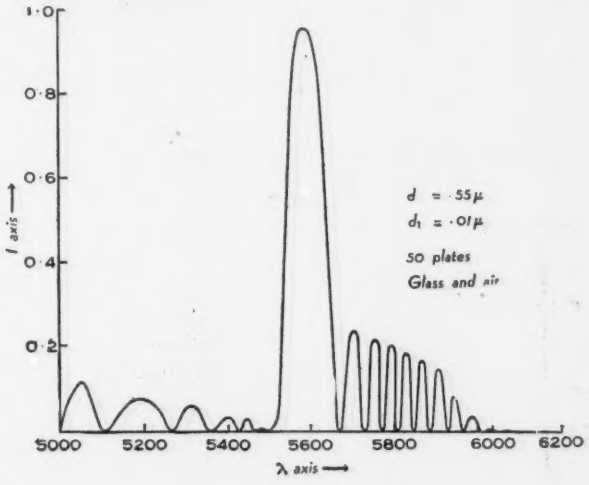


FIG. 5

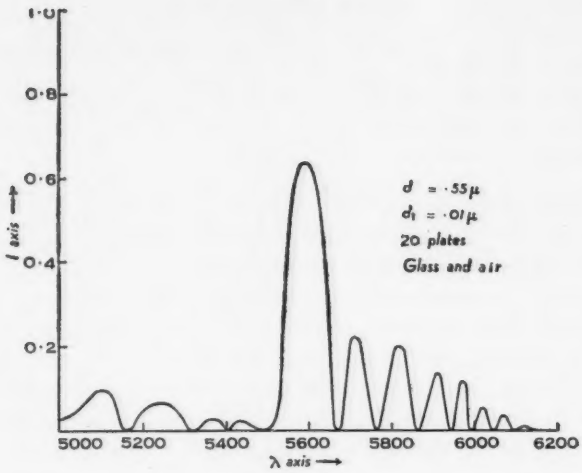


FIG. 6

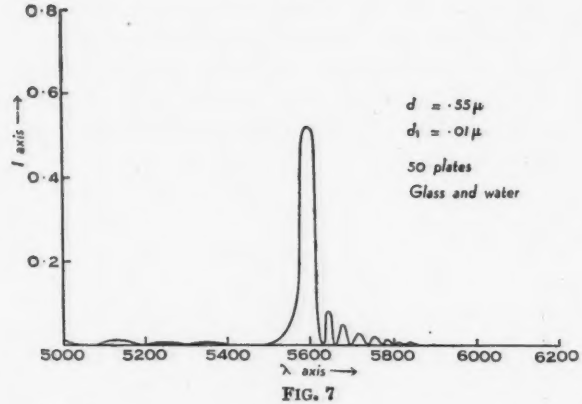


FIG. 7

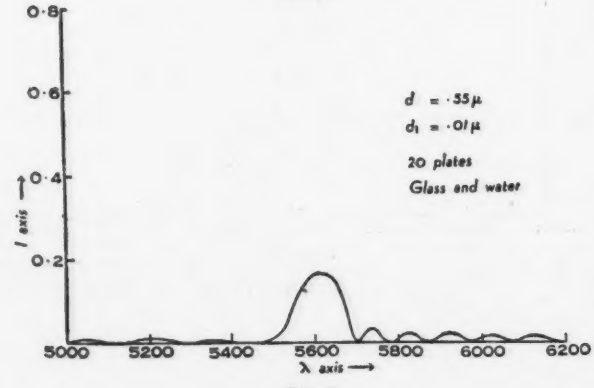


FIG. 8

TABLE IV

Glass and Air						Glass and Water					
λ	$I_{m_{.}=50}$	$I_{m_2=20}$	λ	$I_{m_1=50}$	$I_{m_2=20}$	λ	I_{m_1}	I_{m_2}	λ	I_{m_1}	I_{m_2}
5000	0·0287	0·0262	5620	0·6520	0·6016	5000	0·0099	0·0002	5620	0·1043	0·1452
5050	0·1211	0·0535	5640	0·4270	0·4142	5050	0·0002	0·0097	5640	0·0795	0·0991
5100	0·0023	0·1106	5660	0·1570	0·0957	5100	0·0082	0·0058	5660	0·0149	0·0383
5150	0·0606	0·0121	5680	0·1887	0·0512	5150	0·0052	0·0009	5680	0·0475	0·0013
5200	0·0761	0·0654	5700	0·2455	0·2455	5200	0·0026	0·0092	5700	0·0003	0·0138
5250	0·0321	0·0742	5720	0·0808	0·1932	5250	0·0059	0·0013	5720	0·0373	0·0334
5300	0·0589	0·0021	5740	0·2242	0·1573	5300	0·0009	0·0035	5740	0·0003	0·0315
5350	0·0060	0·0301	5760	0·0561	0·0099	5350	0·0058	0·0051	5760	0·0310	0·0119
5400	0·0382	0·0081	5780	0·2100	0·0818	5400	0·0018	0·0003	5780	0·0001	0·0000
5420	0·0080	0·0366	5800	0·0416	0·1804	5420	0·0024	0·0005	5800	0·0271	0·0088
5440	0·0330	0·0329	5820	0·1966	0·1570	5440	0·0000	0·0020	5820	0·0001	0·0232
5460	0·000	0·0076	5840	0·0696	0·1327	5460	0·0013	0·0012	5860	0·0001	0·0090
5480	0·0035	0·0005	5860	0·1853	0·0055	5480	0·0004	0·0004	5900	0·0013	0·0058
5500	0·0001	0·0001	5900	0·0604	0·0408	5500	0 0000	0·000	5940	0·0034	0·021
5520	0·0382	0·0385	5940	0·1580	0·1449	5520	0·0004	0·0007	5980	0·0064	0·0011
5540	0·5262	0·2433	5980	0·1172	0·1196	5540	0·0050	0·0500	6020	0·0088	0·0130
5560	0·9499	0·4992	6020	0·0866	0·0174	5560	0·0690	0·0700	6060	0·0052	0·0021
5580	0·9625	0·6331	6060	0·0170	0·1378	5580	0·4207	0·0916			
5600	0·9003	0·6573	6100	0·0280	0·0403	5600	0·5193	0·1439			

In conclusion the author wishes to record his grateful thanks to Prof. Sir C. V. Raman, KT., F.R.S., N.L., for his valuable help and inspiring guidance throughout the course of this investigation.

7. *Summary*

By an application of the standard methods of the electromagnetic theory of light, an expression is derived for the intensity of the light reflected from a regularly stratified medium. The intensity and spectral character of the reflected light is computed and discussed for a variety of cases. For small values of the reflecting power, the primary band consisting of the wave-lengths selectively reflected is sharply defined, and accompanied on the longer wave-length side by a number of secondary bands of gradually decreasing intensity. With a reduction in the number of laminæ, the sharpness of the band remains practically unaffected, though the general intensity falls. Below this limit the band begins to broaden. For a given number of plates, the bands are more sharply defined for smaller values of the reflecting power, though the intensity of the reflected light is smaller. Some secondary bands begin to appear on the shorter wave-length side, when the reflecting power is sufficiently large. Further, it is shown that when the reflections from the successive surfaces agree in phase, the smaller the relative thickness of the alternate strata, the larger the number of plates required for complete reflection.

REFERENCES

Drude .. *The Theory of Optics*, Translation by Mann and Millikan, 302.

Wood .. *Physical Optics*, Third Edition, 216.

Rayleigh .. *Proc. Roy. Soc.*, (A), 1917, **93**, 565.

LUMINESCENCE, ABSORPTION AND SCATTERING OF LIGHT IN DIAMONDS: PART I: FLUORESCENCE

By P. G. N. Nayar

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received April 25, 1941

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

The luminescence of diamonds has long been a matter of general knowledge and the literature of the subject goes to papers by Robert Boyle (1672) and Hoffmann (1700). An account of the earlier work in this field is to be found in Vol. V of Mellor's *Treatise on Inorganic Chemistry* (1924). Notable among the investigators of the subject was Sir William Crookes whose monograph "Diamonds" contained much useful information gathered from the study of a large number of crystals. The earlier investigations were however mostly confined to general observations of a qualitative character.

The study of the Raman effect in diamonds has opened a new chapter also in the investigation of the luminescence of diamonds. Ramaswamy (1930) observed a fairly sharp band at 4157 A.U. in the Raman spectrum of diamond recorded by him, and identified it as due to fluorescence. In an investigation of the same subject made with numerous diamonds, Bhagavantam (1930) drew attention to the several features of the fluorescence spectrum and to the fact that the intensity of the band at 4156 A.U. and of the continuous spectrum of longer wave-lengths differ greatly for different diamonds. The work of Robertson, Fox and Martin (1934) should also be referred to in this connection. These authors have brought forward evidence to show that there are two types of diamond distinguished especially by the differences in their ultra-violet and infra-red absorptions. The Raman spectrum also was photographed by them in many diamonds, but only in a few cases were they able to record the fluorescent band at 4156 Å, and they have left the question of its presence in other diamonds an open question.

It is evident from what has been stated that the optical properties of diamond, afford a most interesting field of research. A collection was made by Sir C. V. Raman specially for such an investigation, and a preliminary examination of these diamonds showed most striking variations in the behaviour of the different specimens. The question of the origin of these differences and the interrelation between the different optical properties thus offered itself as a fruitful line of investigation. A careful study was therefore undertaken by the author which included in its scope, the fluorescence and phosphorescence of diamond, absorption in visible and ultraviolet light, the Raman effect in the different crystals, the influence of temperature on these properties and the explanation of the results. The present paper deals with the fluorescent spectra of the diamonds in the collection and with the influence of temperature and the wave-length of exciting radiation on their characters. In subsequent papers the results on phosphorescence, light absorption as well as the Raman effect and a detailed discussion of the interrelation between these phenomena will be presented. Reference may be made here (Nayar, 1941) to a paper on the temperature variation of the Raman frequency of diamond which has recently appeared in these *Proceedings*.

2. *The Material for Study*

12 Diamonds were available for the study. These differed among themselves in their general appearance and properties, some of them showing brilliant luminescence and others hardly any visible effect. To facilitate reference, the diamonds are numbered and described in Table I.

TABLE I

Number	Shape	Dimensions		Colour and Perfection	Visible luminescence under ultra-violet light
		Thickness mm.	Maximum length mm.		
D_1	Triangular flat plate ..	0·76	12	colourless and flawless	absent
D_2	Do. ..	1·22	11	very faint blue tinge cracks and black spots	very strong
D_3	Circular plate	1·39	5	very pale yellow	strong
D_4	Oval plate with facets at the edges	2·21	12	yellow	strong
D_5	Roughly octahedral one set of faces nearly at rt. angles and opposite pairs nearly parallel	2·35	2·35	colourless and flawless	absent
D_6	Cut with many facets ..	2·8	..	colourless with a few cracks	just noticeable
D_7	Do. ..	3	..	pale blue	brilliant
D_8	One half of a natural unpolished crystal	3	..	colourless with reddish inclusions and black spots	faint
D_9	Rod shaped natural crystal	..	2·7	faint pink tinge. Reddish inclusions	faint
D_{10}	Square plate ..	0·97	11	perfectly clear and colourless	just noticeable
D_{11}	Rectangular rod with bevelled edges	1·03	7·5	Do.	faint
D_{12}	Rectangular plate ..	1·2	7·5	Do.	faint

3. *The Fluorescent Spectrum*

Experimental arrangements.—As mentioned above some of the diamonds in the collection showed strong fluorescence. When examined in ultra-violet light, D_7 in particular showed a brilliant blue-green glow and was therefore utilised for the initial experiments. Preliminary observations showed that the fluorescent spectrum extended from 4150 A.U. to longer wave-lengths. To get the full details of this spectrum without interference from the irradiating light, filters cutting off the radiations in this region were introduced in the path of the incident light. A solution of iodine in carbon tetrachloride in a 4 cm. layer of suitable concentration, or Wood's glass were two suitable filters used in these investigations. When used with

a mercury arc, the iodine solution suppresses the 4358 line and longer wave-lengths, the 4046 line providing the exciting source. The Wood's glass filter when used in conjunction with a quartz arc provides the 3650 group of lines for excitation, and the longer wave-lengths are very effectively suppressed.

The arrangement of light-source, crystal and spectrograph adopted as suitable for use with small crystals is described below. The diamond was fixed in a hole in a metal plate and the light from the mercury pointolite lamp was focussed on it through one of the above-mentioned filters. An image of the diamond in fluorescent light was condensed on the slit of the spectrograph in a backward direction. Care was taken to avoid light reflected from the facets of the diamond falling directly on the slit, by suitable orientation of the crystal and the use of screens. A Hilger medium quartz spectrograph of comparatively small dispersion was used in general. A wave-length scale provided in the instrument gave the approximate wave-length directly, but for accurate determinations, a different spectrograph of higher dispersion was employed with iron-arc comparison for measurements.

Results.—The spectrum obtained with the highly fluorescent diamond (D_7) is reproduced in Fig. 1 (*a*), Plate XVI. It can be seen very clearly in the picture that the spectrum consists of a sharp band at 4156 followed by four others, at 4280, 4390, 4515 and 4640 A.U. overlaid by a continuous spectrum. There is also present a very feeble continuum extending to the red. To bring out this part with greater intensity, a picture taken on a Hypersensitive panchromatic plate (Ilford HP_2) with a long exposure is reproduced in Fig. 1 (*b*). The intense part of spectrum is found to extend up to 4900 Å and is followed by a much weaker region extending to about 6300 with concentration of intensity at about 5200 and 6200.

As already mentioned, the sharp band at 4156 has been recorded by Ramaswamy, Robertson, Fox and Martin and by Bhagavantam when photographing the Raman spectra in some diamonds. No mention has however been made by these authors of the very striking set of discrete bands shown in Fig. 1 (*a*) (Plate XVI).

4. Comparison of Different Diamonds

The results of the preliminary observations using a powerful carbon arc and a Wood's glass filter are described in the last column of Table I. The absence of fluorescence in some cases and the fact that earlier investigators have failed to observe fluorescence in many diamonds gives rise to the question whether some of the diamonds are fluorescent at all, and whether the features of the spectrum are the same in all crystals. To settle these

problems long exposures were given using the same experimental technique as was described in the previous section except that filters were dispensed with, and the results are illustrated in Fig. 2 (Plate XVI) and Figs. 3 and 4 (Plate XVII). Due to the difference in shapes it was not possible to give equivalent exposures in all cases but the time taken to register the Raman line was taken as a rough guide of the time of illumination in each case. The case of D_5 was of special interest since no trace of the fluorescent bands could be found in the time taken to record the 1332 line with moderate intensity, but on giving 6 times this exposure, the 4156 band became just visible. The 4-hour exposure (*a*) and the 24-hour exposure (*b*) are shown in Fig. 4 (Plate XVII). It should be mentioned here that the same diamond was used by the author (1941) in a search for weak Raman lines giving exposures up to 120 hours using a spectrograph of larger light-gathering power. In the heavily exposed pictures obtained in the course of that work the presence of the bands referred to already were further confirmed.

Four other cases are grouped together in the increasing order of intensities of fluorescence in Fig. 3 (Plate XVII) and the crystals used are indicated in the figure. With D_{10} and D_6, the photographs show the Raman line with good intensity and the 4156 band and those following it are also about the same order of intensity. With D_8 the fluorescence spectrum is already well recorded before the exposure is sufficient to register the Raman line, and in the case of D_9 the fluorescence is so strong that there is no possibility at all of making out the Raman line in the spectrum. D_{11} and D_{12} were similar to the last mentioned cases, and the pictures were therefore not considered worth reproducing.

A further group of 4 pictures are given in Fig. 2 and are of interest because in this instance the intensities were compared quantitatively by giving equivalent exposures. This was possible because D_1, D_2, D_3 and D_4 were flat plates. The experimental arrangement was the same as that described before, except that the plates were cemented on black glass to suppress the reflection of incident light from the back surface. To allow for the differences of scattering volumes, the times of exposure were made inversely proportional to the thicknesses, with a further correction by the Schwartzchild factor to allow for the non-linearity of photographic blackening with time. The spectrograph slit was kept rather wide to reduce the exposure time as it was essential to keep the current and voltage of the lamp constant throughout.

It can be seen readily from the Plate that the spectrum is similar in all cases, even though it is recorded only very weakly in the case of D_1. The

intensity on the other hand varies, the visual estimate of intensities of D_2, D_3, D_4 and D_1 being in the order 100, 60, 50 and 1. While there is no particular point in knowing the exact value of this ratio, the order of intensities obtained in a strictly comparable manner is of help in correlation with other properties.

The range of intensity difference of the order of 100: 1 between D_2 and D_1 is striking enough. But considering the fact that the fluorescence in D_7 appeared to be about 10 times more intense than D_2, and in D_5 appeared to be much feebler than that of D_1, the ratio of its intensity between the two extreme cases, namely D_7 and D_5 available in the collection appeared to be very great. Unfortunately the shapes of the crystals did not permit a quantitative comparison to be made but a rough estimate made from the times of exposures necessary to record the fluorescence D_7 and D_5 point to a ratio of intensity of the order of 10,000: 1.

The spectroscopic examination of the 12 crystals in all, shows very clearly that *a fluorescence spectrum consisting of a band at* 4156 Å *and a number of discrete bands superposed on a continuous spectrum are present in every diamond crystal. The intensity of the fluorescence, on the other hand, is capable of varying between different diamonds to an enormous extent,* the two extreme cases in the collection used for these experiments showing a difference of as much as 10,000: 1.

At this stage it might be considered whether there is any obvious relationship between the fluorescent property of the different crystals and their colour and appearance. The two most strongly fluorescent specimens show a pale fugitive blue tinge while the specimens in which fluorescence is specially weak are colourless. Bhagavantam has made the interesting suggestion in his paper that the blue colour in diamonds is fluorescent in origin. The author has examined some specimens of the well-known Blue Jaeger variety which show a fine play of blue colour and found that they invariably show brilliant fluorescence in ultra-violet light. Bhagavantam found that a yellow diamond did not give the 4156 band but in the present collection D_4 which is of a prominent yellow colour and D_3 of a pale yellow colour have both been found to give the bands quite strongly. The method of observation of the front surface of the crystal employed in the present investigations partly overcomes the difficulty due to absorption of the violet region by yellow crystals.

It can therefore be stated that the absorption colour and visible inclusions do not bear any relation to the intensity with which a diamond fluoresces, but that on the other hand, when the fluorescence is sufficiently intense, it gives the diamond a bluish tinge.

5. *Effect of Wave-length of Exciting Light*

Experimental.—It is well known that fluorescence of a substance is excited only when the wave-length of irradiating light is less than the short wave-length limit of the fluorescent bands. As has been mentioned already, the fluorescence in diamonds starts from about 4156 A.U. and extends towards the red end of the spectrum. It could be seen by using suitable filters that the mercury line 4046 excites the emission very strongly and that no visible effect is produced by the 4358 line alone. Since these two lines cover a region of wave-lengths too wide apart, use was made of a monochromator arrangement to study the effect of varying the exciting wave-length in small steps.

A Hilger Constant Deviation Spectrograph served very satisfactorily as a monochromator. The light from a source of white light was spread out into a spectrum by the constant deviation prism and thrown on a screen in which a slit was provided. The image of this slit was focussed on the diamond and the light given out by the crystal was caught at a suitable angle and condensed by a lens on the slit of the medium quartz spectrograph. As usual, the crystal had to be carefully oriented to avoid direct reflections falling on the slit.

A carbon arc was used for initial visual adjustments. A source of light more convenient for giving long exposures was found in the new type of gas-filled coiled-coil lamp in which the whole luminosity is concentrated in a short straight filament. When over-run at 30% more than the specified voltage, these lamps gave very satisfactory intensity in the violet and near ultra-violet region.

With this arrangement, a nearly monochromatic beam of light of about 40 Å breadth could be used for illuminating the diamond, and the required wave-length could be obtained by simply turning the drum head of the wave-length scale. To reduce exposure time the spectrograph slit was kept as wide as could be done without sacrificing essential details of the spectrum. The exposure time was initially adjusted to show the spectrum resolved into its component parts with moderate intensity when the illumination was by a beam of wave-length 4,000 Å.

Results.—The effect of changing the exciting wave-length from 4000 Å to 4225 Å in four steps is illustrated in Fig. 5 (Plate XVIII). The highly exposed line represents the excitation, and the fluorescent bands can be recognised easily in the pictures. In the first picture of the series, the excitation is by a beam of wave-length 4000 Å (mean) and when this is changed to 4125, there is a diminution of intensity throughout the spectrum.

When the exciting wave-length is made to coincide exactly with the first fluorescence band at 4156, there is a considerable brightening of the bands which follow it. In the last picture of the series, the exciting beam has crossed to the longer wave-length side of 4156, and all the bands are found to be extinguished.

The exposures were the same from the point of view of time in all cases, but no allowance had been made for the variable distribution of energy in the spectrum of the source from which the monochromatic beam was isolated. However, the incandescent lamp used had a perfectly continuous spectrum, and the difference of intensity between two neighbouring regions at 4125 Å and 4160 Å is not sufficient to account for the considerable rise of intensity that is observed. There is therefore a true resonance effect when the exciting wave-length coincides with the band at 4156 Å.

It can be inferred readily that the entire spectrum is fundamentally related to the band at 4156 Å. The disappearance of all the bands when the exciting wave-length is longer than 4156 following Stokes's law, as well as the resonance effect when illuminated by light of wave-length 4156 establish *that the* 4156 *band is the "head" of the entire system of fluorescent bands.*

Extension to shorter wave-lengths.—Using a small quartz spectrograph and the same arrangements as described before, an attempt was made to extend the study to the ultra-violet region. Due to the lack of a suitable continuous source of light and insufficient light gathering power of the small quartz spectrograph used as monochromator, this region could not be satisfactorily explored from the point of view of intensities. It was found however that the same fluorescence spectrum could be excited by wave-lengths down to 2900 Å. No evidence of any further bands in the ultra-violet was found with moderate exposures, and the difficulties mentioned above prevented a complete investigation.

6. *The Influence of Temperature*

Experimental.—Having recognised that the nature of the spectrum is the same in all diamonds except for variations in the intensity, an accurate analysis of the frequencies at different temperatures was carried out. A Zeiss 3-prism glass spectrograph with the long camera attachment giving a dispersion of about 26 Å/mm. in the 4358 region was used for this investigation. A diamond of strong fluorescing power (D_2) was used and the effect of temperature on the wave-length and intensity was simultaneously studied from liquid air temperature up to 200°.

To obtain a reliable comparison of the intensities in different cases, it is necessary to keep the position of the crystal undisturbed for all the exposures. The experimental arrangement adopted to attain this end is described below:

The crystal (D_2) was mounted in a small copper block in which a thermo-junction was embedded, and held close to the side of an unsilvered pyrex Dewar flask. The mercury light filtered through a solution of iodine in carbon tetrachloride was focussed on the crystal and the fluorescent light collected on to the spectrograph slit in the usual way. A well exposed picture at room temperature was obtained in $2\frac{1}{2}$ hours.

The flask was then filled with liquid air filtered through glass wool, to remove suspended particles of ice. The same exposure as before was given keeping the lamp current and voltage constant. After the low temperature exposure was completed, the remaining liquid air was allowed to evaporate and a small heating coil was introduced inside the flask. By keeping the mouth of the flask closed and passing a current through the coil, the flask was made to serve as a hot air thermostat, the actual temperature of the crystal being shown by the thermocouple. A series of exposures up to 200° were given on the same plate.

Since the pictures are taken under identical conditions on the same plate, the comparison of intensities at different temperatures is reasonably accurate. When the crystal is immersed in liquid air however, the loss of light by reflection is slightly reduced with the result that the effective intensity of illumination is slightly enhanced. The absorption due to liquid air at 4750 is pointed out in the photograph.

Results.—In Fig. 6 (Plate XIX), the spectra at different temperatures are reproduced and the prominent features are marked out in the picture at liquid air temperature. Since much greater details of the structure of the prominent bands as well as the intermediate regions are available at $-180°$, the results obtained at this temperature are first described.

TABLE II

Fluorescence at Liquid Air Temperature

Note.—The limits of the bands where they are indefinite are enclosed in brackets. The positions of the intensity peaks are shown in heavy type. The principal bands are numbered I, II, III, IV, V, and the intermediate regions are numbered (i), (ii), (iii), (iv).

No. of band	Wave-length in A.U.	Remarks
(i)	4118 to 4127	Very faint (double structure)
I	4151 **4153** 4256	Beginning of band Intensity peak
(ii)	(4175) (4184) **(4206)** (4227)	Faint diffuse Lines
II	4247 **4275** 4294 (4311)	Sharp edge Int. max. Sharp edge Int. max.
III	(4365) **4381** **4397**	Edge of band. Int. max. followed by a gap and another int. max. terminating in a sharp edge.
(iii)	(4404) 4419 (4470)	Faint diffuse band
IV	(4483) **4510** (4528)	
V	(4620) **4638** (4670)	
(iv)	Continuous spectrum up to about 4950	Concentration of intensity between 4800 to 4900—just noticeable

In the table, the prominent bands are numbered I to V. Before the first prominent band, there is a faint band with a split structure in the region 4118 to 4127. This is extremely faint, and has not come out clearly in the reproduction in Fig. 5, but in the heavily exposed picture in Fig. 1, the

band can be noticed as a concentration of intensity just preceding the main band at 4156. The details of this band are just visible in the liquid air picture but are not very clear in the other photographs.

The first prominent band which is the most interesting feature of the diamond spectrum is extremely sharp. The band is roughly 5 Å in breadth between the extreme limits and at $-189°$, the peak of intensity is at 4153. This is followed by a faint band which at $-180°$ is clearly resolved into diffuse lines at 4175, 4184, 4206 and 4227 of which the one at 4206 is the most prominent. Companions to the 4156 band at 4131, 4175, 4186 and 4196 at room temperature have been reported before by Bhagavantam.

The II band starts with a sharp edge at 4247, rises to a greater intensity between 4275 and 4294 where there is a sharp edge. This is followed by a diffuse region terminating at about 4311 Å.

The III band also shows a double structure. The band is diffuse on the short wave-length side near 4365 and rises to maximum intensity at 4381. This is followed by a small gap and again a rise of intensity terminating in a sharp edge at 4397 Å.

After the III band, is a faint diffuse band roughly between 4404 and 4470 with a peak at 4419. (A spectrograph "ghost" appears in this region and is marked as such in the photograph.)

The IV band is very diffuse and no structure can be noticed. It extends from about 4483 to 4528 and has a maximum of intensity at 4510.

The V band also is very diffuse extending from 4620 to 4670 with the peak at 4638.

After this, there is a region of continuous spectrum, the details of which cannot be determined with certainty.

Room Temperature and Higher Temperatures.—The values of the wave-lengths of the different bands at these temperatures are given below in Table III. The bands are numbered as in the previous table. Since at these temperatures the details of the bands are not clear enough for measurement, only the positions of the intensity maxima are shown.

TABLE III

Fluorescence at Temperatures from 25° *to* 200°

Band No.	Temp. °C.			
	25°	60°	150°	200°
(i)	(4132)	..	..	..
I	4156	4157	4161	4162
(ii)	4209	4212	4219	4222
II	4278	4280	4287	4296
III	4387	4390	4400	4406
(iii)	Too faint to be measured			
IV	4514	4518	4522	4526
V	4643	4645	4650	4658

At 25° the preliminary band which appears at − 189° between 4118 and 4127 is not noticeable except for a slight concentration of intensity at approximately 4132.

The I band at 4153 shifts to 4156 and has broadened out a little unsymmetrically towards the red. The faint band following this has become too diffuse and corresponding to the line at 4206 there is a concentration of intensity at 4209. The second band also loses the sharp edge at 4277 and appears to begin at 4250. instead.

In the III band, the peak has shifted to 4390 and the double structure of the band found at − 189° is hardly noticeable.

The IV and V bands which are comparatively diffuse even at liquid air temperature become still more so and the peaks appear to shift to 4514 and 4643.

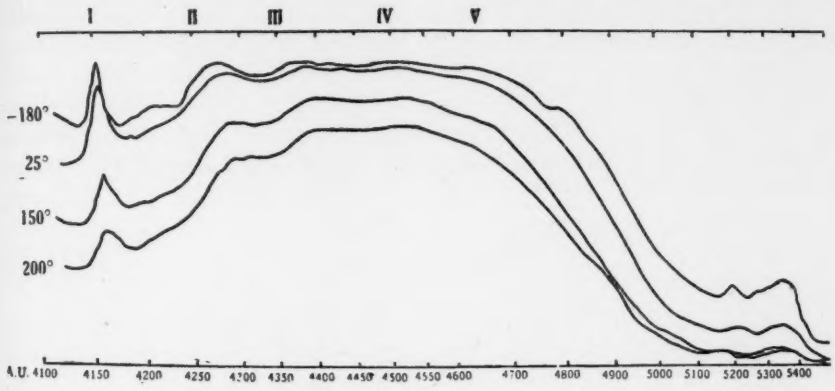


FIG. 1

To follow the changes at higher temperatures, where the bands are too diffuse, the microphotometer tracings are more helpful. The curves show fall of intensity, shift in frequency ard broadening of the bands in a striking way but the details of the individual bands are not rendered very clearly by the microphotometer due to high density of the pictures. Attention may be drawn to the fact that at liquid air temperature the band at 4153 Å has a symmetrical shape and that it broadens unsymmetrically towards the long wave-length region as the temperature is raised.

Though the entire spectrum undergoes a diminution of intensity as we proceed to higher temperatures, the fall of intensity is not the same for all regions of the spectrum. In this respect the principal band at 4156 stands out separately, falling off at a more rapid rate than the others which behave alike in this respect.

It can be seen from the curves that two separate effects are responsible for the fall of intensity itself. Since the bands broaden at higher temperatures, the energy is distributed over a wider region of the spectrum. In addition, there is also a loss of intensity as a whole, so that at 300° there is practically no fluorescence. Since it is not possible to get the integrated intensity from the contour of each band due to overlapping of the continuous spectrum, a quantitative estimate of the variation of intensity with temperature could not be undertaken.

The results obtained in this section show that temperature influences the fluorescence spectrum to a considerable extent. These changes which are strikingly shown in the microphotometer curves and the photographs

in Fig. 6 have four distinct features. (1) The bands broaden unsymmetrically and become more diffuse as the temperature is raised. (2) The bands are shifted to longer wave-lengths, the principal band undergoing a shift from 4153 Å at liquid air temperature to 4162 Å at 200°. (3) The intensity falls off rapidly, and at 300° the bands practically disappear. (4) The relative intensity of the bands undergo changes, the principal band at 4156 falling off in intensity at higher temperatures at a more rapid rate than the other portions of the spectrum.

7. *Discussion*

Several new facts regarding diamonds have emerged from the experimental work described in this paper. Starting from the evidence available from previous investigations of the presence of a fluorescent band at 4156 Å, it has been shown that this frequency is present in every diamond. The intensity however is found to vary between different crystals to an enormous extent, and this explains the failure to observe this frequency by earlier workers in some very weak cases like that of D_5 described in this paper. The origin of the fluorescence is a question which is discussed in detail later on after the results on light absorption and other related matters are dealt with, but at this stage it may be pointed out that the presence of the band in every case and extent to which the intensity can vary in different crystals is an indication that the origin of the fluorescene is connected with the structural perfection and not to any extraneous impurity.

The weak part of the spectrum extending to 6300 Å has been given only minor attention in this paper. That this part is of importance in *Phosphorescence* will be shown in a subsequent paper. Regarding the bands newly observed, their close connection with the band at 4156 has been established in the studies with different exciting wave-lengths. The failure of other workers to observe these bands is probably due to their not having obtained clear pictures with the use of filters. However in the photographs published by Bhagavantam, there are indications of their presence.

A frequency at 4156 Å has been observed by John (1931) in cathode luminescence, and Walter and others in absorption. The author's investigations on absorption of light show further experimental evidence connecting absorption to fluorescence, and the significance of these frequencies are left for detailed discussion in further papers on the subject.

The author's best thanks are due to Professor Sir C. V. Raman for the loan of the diamonds and his helpful interest and suggestions in this work.

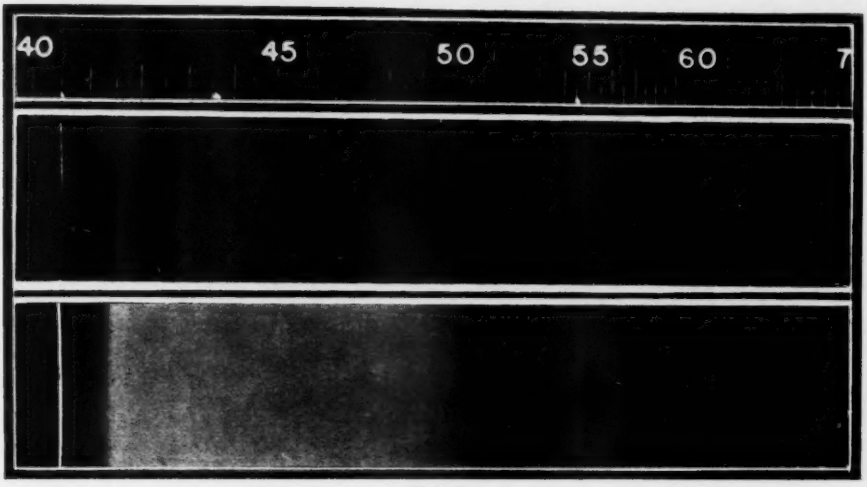


FIG. 1

Fluorescence Spectrum of Diamond (D_1)

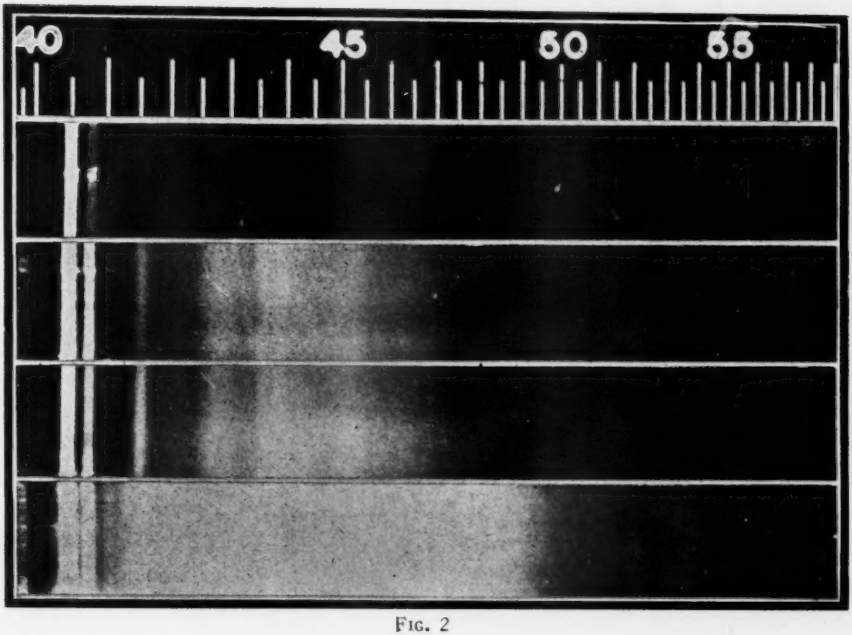


FIG. 2

Fluorescence in different Diamonds

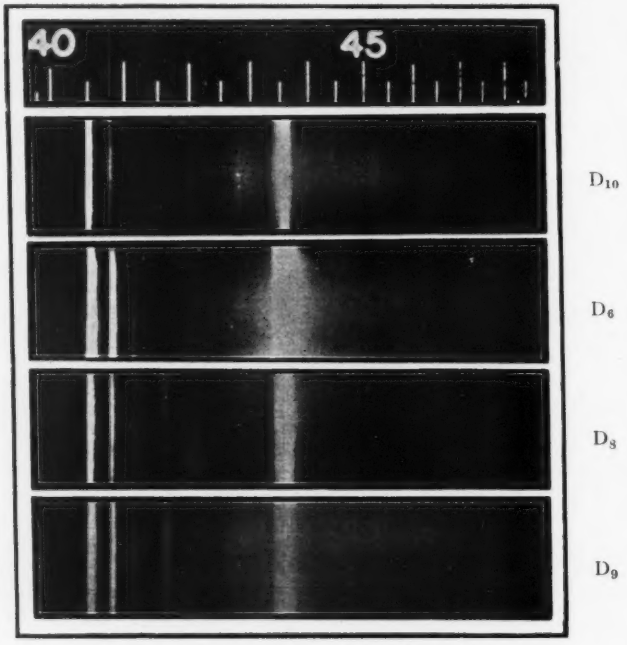


FIG. 3. Fluorescence in four Diamonds

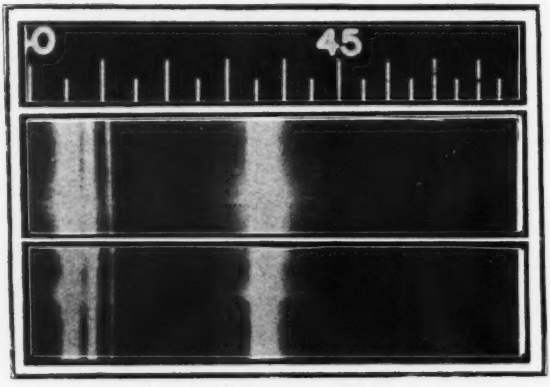


FIG. 4. Fluorescence in D_5

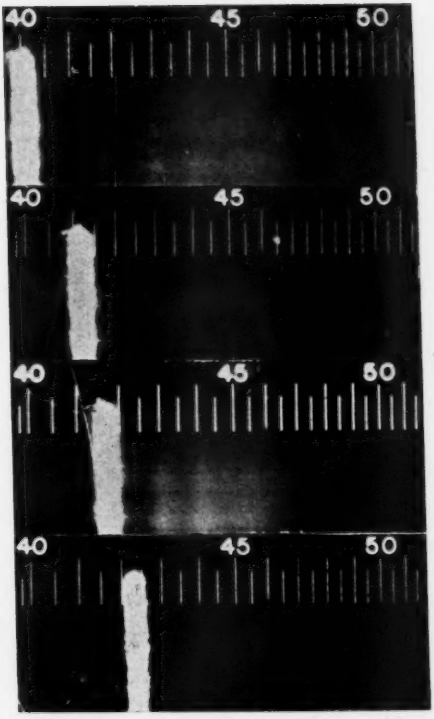


FIG. 5. Fluorescence Excitation by different Wavelengths

Fig. 6. Illustrating Stark-effect of Diamond at different Temperatures.

8. *Summary*

This paper which is the first of a series on the luminescence and absorption of light in diamonds, deals with a study of fluorescence in a collection of crystals differing widely in their properties. Studied with filters, the spectrum is found to consist of a sharp band at 4156 Å, followed by a set of discrete but rather diffuse bands at 4278, 4387, 4514 and 4643 Å, with a feeble continuous spectrum superposed on these extending to 6300 Å. As a result of investigations directed to this question, it has been found that these frequencies are present in all crystals. However, the intensities of fluorescence in different diamonds vary to an enormous extent. In the collection studied, some showed brilliant fluorescence, while others required long photographic exposures to record the presence of these frequencies. The two extreme cases in the collection showed a difference of the order of 10,000 to 1.

The entire spectrum can be excited by light of any wave-length less than 4156 Å, but is found to brighten up and then disappear according as the wave-length of excitation is made equal to and then greater than 4156, thus indicative of a resonance effect. The presence of this frequency in every case, and its remarkable variation in intensity is pointed out as suggesting that these frequencies are independent of extraneous impurities and are probably connected with the structural perfection of diamonds.

The effect of temperature on the bands has been studied from $-180°$ to 200° C. The bands are found to shift in frequency and broaden unsymmetrically towards longer wave-lengths as the temperature is raised. The fluorescence disappears at higher temperatures, the band at 4156 falling off in intensity at a more rapid rate than the other bands.

REFERENCES

Bhagavantam, S.	..	*Ind. J. Phys.*, 1930, **5**, 169 and 573.
Crookes, W.	..	" Diamonds," Harper Bros., London.
John	..	*Ind. J. Phys.*, 1931, **6**, 305.
Mellor	..	*Comprehensive Treatise on Theoretical and Inorganic Chemistry*, 1924, **5**, 768–79.
Nayar, P. G. N.	..	*Proc. Ind. Acad. Sci.*, 1941, **13**, 284.
Ramaswamy, C.	..	*Ind. J. Phys.*, 1930, **25**, 97.
Robertson, R., Fox, J. J., and Martin, A. E.		*Phil. Trans. Roy. Soc.*, 1934, **232**, 494.

EFFECT OF ADMIXTURE OF SILVER ON THE RECTIFYING PROPERTIES OF Cu-Cu_2O CELLS

By K. R. Dixit

(Gujarat College, Ahmedabad)

Received May 27, 1941

(*Patent applied for*)

Numerous 'Sperrschicht cells' or 'Barrier-layer rectifiers' are in commercial use; and it is very likely that this extremely useful device in its many forms will be increasingly employed to supply the demands for the direct current throughout the electrochemical and electrometallurgical industries. Unfortunately the precise details of construction have not been published,[1-3] nor are we familiar with the manner in which the physical conditions affect the rectification. This state of affairs results in the absence of a satisfactory theory of the rectifier action. In this field no material seems to have been studied more extensively than the copper-cuprous oxide rectifier; but even this material has not been the subject of a systematic investigation. We have undertaken to study systematically the various factors which alter the rectification of copper-cuprous oxide layers with a view that such a systematic knowledge will enable us to understand the mechanism of the rectifying action. In this paper the influence of a small percentage of silver impurity included in the copper block on the rectification is reported. But before we proceed to describe the experiments and their significance it would be better to give an outline of our present knowledge—both experimental and theoretical—of the Cu–Cu_2O cell.

A typical rectifying contact consists of a metal separated by a very thin almost insulating layer from a good semiconductor.[4-11] The Cu–Cu_2O rectifier is made by oxidising one face of a block of chemically pure metallic copper to an appreciable depth. The oxidation takes place in an electrical furnace at a little over 1,000° C. The block is usually polished flat before oxidation; this helps in making a good contact during its subsequent use. The oxidation converts the copper to Cu_2O. The cuprous oxide next to the mother copper is almost pure, but the subsequent layers are rich in oxygen. The pure Cu_2O forms the insulating layer and the pure cuprous oxide with the extra oxygen is a good impurity semiconductor. For efficient working the insulating layer should be about 10^{-5} cm. thick. Such plates are usually pressed together in a pile and possess another contact between the semiconductor ($Cu_2O + O$) and metallic lead. This contact between a good

semiconductor and a metal does not rectify appreciably. The efficiency of a rectifier is usually expressed by the ratio r_2/r_1, r_2 and r_1 being the resistances observed when the current passes in the unwanted direction and in the wanted direction respectively, both resistances being measured at the same voltage.

The conduction electrons in a crystal lattice are supposed to occupy a band or a series of bands of energy levels.[12–20] If the bands are completely filled there can be no conduction. A semi-conductor is formed when a new distinct band or set of levels of intermediate energy is supplied by the impurities present. In the system metal/semi-conductor/metal the two contacts are quite different, one forming an appreciable gap across which current has to flow and the other being a very intimate contact. If the potential of the metal is raised by V, the current transmitted across the gap can be obtained by applying the Schrödinger equation. Current $= \alpha\epsilon^{-\beta V}\{\epsilon^{eV/kT} - 1\}$ where α and β are constants. The current in the reverse direction will be $\alpha\epsilon\beta V\{1 - \epsilon^{-eV/kT}\}$. The passage of the electrons across the potential barrier is explained in the above theory by the quantum-mechanical 'Tunnel effect'. But according to Mott[21,22,25] such a theory predicts a wrong direction of rectification; and he points out that the correct direction is secured by assuming that the electrons are able to go over the potential barrier when they are thermally excited, and not through it by the 'Tunnel effect'. Schottky[24] compares the metal/semiconductor/metal rectifier with a discharge tube working at low pressures. The metals take the place of the electrodes and the semiconductor of the space charge between the electrodes. The assumptions of Mott and Schottky are essentially similar and would give similar expressions for the current.[21–25]

Procedure

Copper used in these experiments, was obtained from 100% pure copper wire (B. G. No. 14, made in Germany) available locally in ½ lb. bundles. The silver was commercially pure silver, also available locally at a silversmith's. The alloys were prepared by melting ½ lb. of copper and the required amount of silver. The solid blocks were hammered to give plates about 3 to 4 mm. thick. The following plates were prepared in this way, Pure copper, 2½% Ag in Cu, 5% Ag in Cu, · · · · ·, 20% Ag in Cu.

The furnace was an electrical one prepared by winding No. 18 Nichrome wire. The temperatures were measured by a platinum-rhodium thermocouple and a calibrated millivoltmeter. The blocks were heated in a porcelain tube in vacuum, a hyvac pump was running all the time. The oxidation of the blocks was carried out by admitting air at a definite

pressure. The air was admitted through a capillary tube and was pumped out by the pump. This enables us to maintain a constant flow of air at a definite pressure. The pressure can be adjusted to any desired value by choosing a suitable length and diameter of the capillary tube as well as by changing the pumping speed.

The porcelain tubes used for heating were selected from those used by electrical wiremen for taking wires through walls, etc. Only such tubes were chosen as could stand vacuum at high temperature. The glazing material used for coating the inside of such tubes by the manufacturers decomposed and caused some trouble. This difficulty was overcome by baking the tube for half an hour at 1,100° C. Such tubes are quite satisfactory and can very well replace the silica tubes used in similar experiments.

The porcelain tube is sufficiently long so that the two ends are well out of the furnace and are closed by rubber stoppers. In any experiment two blocks either of pure copper or one of pure copper and the other of alloy were placed at the centre of the furnace. The two blocks should not touch one another, otherwise silver from the alloy diffuses into pure copper. (This actually happened in one case, the silver creeping all along the surface of pure copper at a temperature of 800° C.) The blocks were reasonably flat, and were preapred by polishing them successively on 1, 2, 3 and 4 zero emery paper, with benzene or ether.

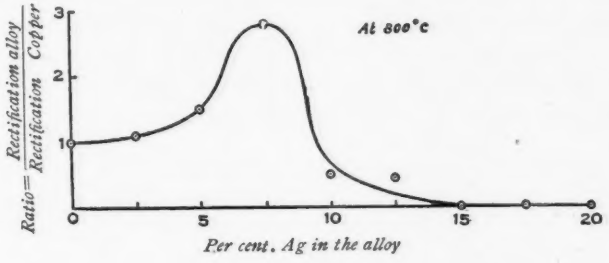
The layers of the oxide were formed in most cases by allowing air at 4 cm. pressure to flow intermittently for about 6 minutes. The blocks were allowed to cool down *in situ* to a temperature of 500° C., then they were taken out of the vacuum and cooled further by dropping in water. The layers formed at temperature of 750° C. and more adhered firmly to the base, whereas those formed at 700° C. and less peeled off easily on dropping in water, but did not peel off when cooled inside the vacuum system. The firmly adhering layer sticks so well that it can be removed only by filing.

In our arrangement the oxide layers are formed on both sides of the block. The coating on one side is filed off by holding the specimen in a vice. The remaining layer is pressed against a lead block and the resistance is measured in both directions by applying a difference of potential of two volts. On dropping in water a layer of cupric oxide is usually formed on the surface, this was removed by gently rubbing the face on ether and 2 or 4 zero emery. The thickness of such a rectifying layer is of the order of one-hundredth of a millimetre and the resistance in the low resistance direction is of the order of 500 ohms/cm.[2]

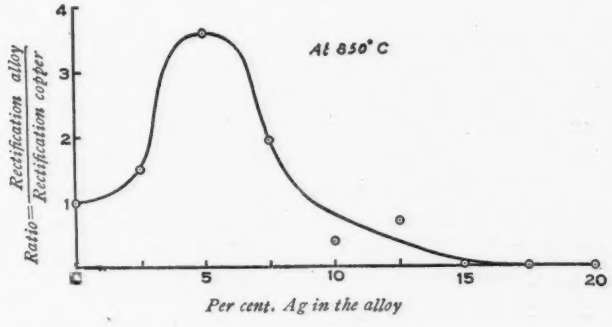
Results

Copper blocks made from the same plate and treated under exactly identical conditions of temperature, pressure and cooling do not show identical rectification. The rectification is distributed about a mean value according to the Gaussian Law. Copper blocks prepared at about 600° C. just begin to show a perceptible rectification. The rectification goes on increasing apparently according to an exponential law as the temperature at which the layer is formed goes on increasing. This work has been done in our laboratory by Mr. S. G. Sharangpani and will also be soon published.

Curves I and II.—The layers formed on alloys at 900° and 950° C. show the well-known phenomena of ' spitting ' and the rectifying action of such blocks could not be measured. The layers were formed on alloys at 700° C., 800° C. and 850° C. and the rectifying action of these layers was compared with that of a layer formed on pure copper under identical conditions. The rectification as will be seen from Curves I and II goes on increasing at first as the percentage of silver increases, reaches a maximum at about 5 to 7% of silver and then diminishes and practically becomes zero for about 12% of silver.



CURVE I



CURVE. II

The rectifying action of pure copper at these temperatures (700° C.–850° C.) is very small and lies roughly between 2 and 4. Whereas the rectification at 850° C. of 5% alloy can be as high as 15—a rectification which can be obtained with pure copper only if the temperature of the formation of the layer is about 1040° C.

Discussion

Copper and silver are both similar metals and crystallise in similar systems. The presence of a small amount of silver in the metallic copper is not likely to change its properties appreciably; even the lattice constant changes only by about 1% after the addition of 7% silver.[26] But it is quite likely that the electronic levels in consequence of the different atomic volumes of copper and silver are profoundly modified.[27] This modification is likely to allow a large number of electrons to go over the potential barrier. The large effect obtained with an alloy can be obtained with pure copper when the temperature of formation is increased considerably. It is but natural to expect that the modification of electronic energy levels produced by an impurity will go on increasing as the amount of impurity increases, and as a result the rectification should also increase with the impurity. But this is not observed to be the case, the rectification actually decreases when the amount of impurity increases beyond a limit. It may be that in such a case the unfilled bands overlap to such an extent that the direction of unrestricted motion is no longer a preferential direction.

Further some atoms of silver which are present along with the copper may be oxidised. Thus in addition to oxygen, silver oxide may be present as an additional impurity in the impurity semi-conductor Cu_2O. But when the amount of this impurity increases beyond a limit, it apparently no longer gives rise to a unidirectional current.

In this connection it is worth noticing that silver and copper are perfectly miscible in the liquid state but at a temperature of 779° C. only 7% of Ag is soluble in copper.[28] This probably means that at this temperature only 7% Ag can be included as an isomorphic inclusion in the copper lattice and is able to produce a maximum modification of the electron levels. Further if we consider a group of 27 elementary cells of copper, we see that the minimum number of silver atoms which can be included and will influence all these cells is 8. This gives a ratio of 8 Ag atoms to $27 \times 4 = 108 - 8 = 100$ Cu atoms as the ratio which is likely to give a maximum modification of the electron levels.

These experiments carried out with rectifying layers formed on pure copper and Ag-Cu alloy blocks appear to indicate that the process of rectification is probably governed by statistical laws.

Summary

The effect of including silver in copper blocks on which rectifying layers of Cu_2O are formed is determined experimentally. The rectification is maximum for 7½% Ag when the temperature of formation of the layer is 800° C., but if the temperature of formation is 850° C. the maximum rectification is obtained with 6% Ag inclusion. It appears that the rectification is probably governed by statistical laws.

REFERENCES

1. Bergmann, L. .. *Phys. Zeit.*, 1932, **33**, 209.
2. Grondahl, L. O. .. *Rev. Mod. Phys.*, 1933, **5**, 141.
3. Lange, B. .. *Die Photoelemente und ihre Anwendung*, Barth/Leipzig, 1936.
4. Wilkins, F. J. .. *Proc. Roy. Soc.*, 1930, A, **128**, 407.
5. Bulian, W. .. *Phys. Zeit.*, 1933, **34**, 745.
6. Barnard, G. P. .. *Proc. Phys. Soc.* (*London*), 1935, **47**, 477.
7. Schottky and Waibel .. *Phys. Zeit.*, 1935, **36**, 912.
8. Grondahl, L. O. .. *Trans. Elektrochem. Soc.*, 1937, **72**, 225.
9. Nölge, H. .. *Phys. Zeit.*, 1938, **39**, 546.
10. Levinzon and Dunaev .. *J. Tech. Phys.* (*U.S.S.R.*), 1938, **8**, 1212 (available only in abstract).
11. Dubar, L. .. *Ann. de Physique*, 1938, **9**, 5.
12. Nordheim, L. .. *Phys. Zeit.*, 1929, **30**, 177.
13. Georgeson, W. .. *Proc. Camb. Phil. Soc.*, 1929, **25**, 175.
14. Wilson, A. H. .. *Proc. Rov. Soc.*, 1932, A, **136**, 487.
15. Nordheim, L. *Zeit. f. Phys.*, 1932, **75**, 434.
16. Frenkel and Joffe .. *Phys. Zeit. Sowjet*, 1932, **1**, 60.
17. Bornstein, M. .. *Ibid.*, 1933, **2**, 28.
18. Fowler, R. H. .. *Proc. Roy. Soc.*, 1933, **A, 141**, 56.
19 Wilson, A. H. .. *Theory of Metals*, 1936, Cambridge.
20. Fowler, R. H. .. *Statistical Mechanics*, 1936, Cambridge.
21. Mott, N. F. .. *Proc. Camb. Phil. Soc.*, 1938, **34**, 568.
22. ———— .. *Proc. Roy. Soc.*, 1939, A **171**, 27.
23. Hilsch and Pohl .. *Zeit. f. Phys.*, 1939, **111**, 399.
24. Schottky, W. .. *Ibid.*, 1939, **113**, 367.
25. Mott and Gurney .. *Electronic Processes in Ionic Crystals*, 1940, Oxford.
26 Weist, P. .. *Zeit. f. Phys.*, 1932, **74**, 225.
27. *Handbuch der Metallphysik*, Leipzig, 1935, 1937.
28. Tammann, G. .. *Lehrbuch der Metalkunde*, Leipzig, 1932.

ON THE PREPARATION OF QUARTZ ULTRASONIC OSCILLATORS

By Dr. R. R. Bajpai and Dr. V. I. Vaidhianathan
(*Irrigation Research Institute, Lahore*)

Received March 31, 1941

In certain problems connected with the detection of cavities under weirs it became necessary to generate powerful ultrasonic radiations in this Institute. The first important step in this connection was to prepare thick X-cut crystals from natural quartz; for firstly, these are costly to import and, secondly, due to war conditions they cannot be obtained in any reasonable period. A technique has, therefore, been developed to prepare the required crystals from natural ones.*

Geometry of the Crystal

A quartz crystal may roughly be said to be a hexagonal prism terminating at either end in apparent hexagonal pyramids. Fig. 1 shows a perfect left-handed crystal and Fig. 2 a right-handed one. The crystals possess

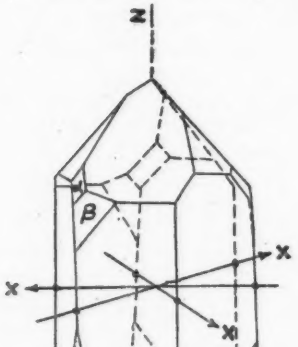


Fig. 1
Left-handed Quartz Crystal

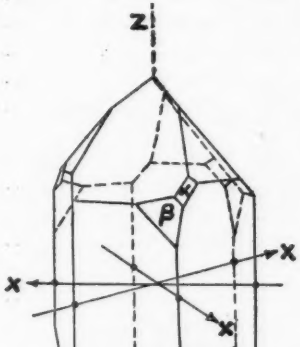


Fig. 2
Right-handed Quartz Crystal

* Natural quartz was very kindly supplied to us by Dr. C. S. Fox, Director of the Geological Survey of India.

trigonal symmetry about the line joining the vertices of the pyramids at either end, so that the prism and pyramid faces are similar only alternately. This line is the optical, trigonal or principal axis and is generally called the Z-axis. The crystal further possesses three axes of diagonal symmetry, in a plane at right angles to the principal axis. These are known as the electric or the X-axes and are perpendicular to the Z-axis and connect in every case two opposite edges of the six-sided prism, which, however, are not similar.

For piezo-electric work three more axes, coplanar with and perpendicular to the diagonal axes, have been assumed. These are known as the Y-axes and have no crystallographic significance.

Selection

Quartz suitable for piezo-electric work must not have the following defects:—

(1) Optical twinning. (2) Electric twinning. (3) Presence of clouds, cracks, or bubbles and (4) Inclusion of foreign materials.

These defects are detected as follows:—

As stated above quartz is of two types—left-handed and right-handed. This is due to the atomic structure of the crystal which has got a spiral arrangement in the direction of the Z-axis. It is the direction of rotation of the spiral which is responsible for the type of the crystal. These types can generally be distinguished by looking to the direction of the subsidiary faces marked α and β in Figs. 1 and 2 or optically. Sometimes both the types of structures get intermingled in the same specimen. Such a crystal is said to be optically twinned. A rough test for the detection of this form of twinning is that the horizontal striæ on the prism faces which are parallel in the case of a good specimen become broken by means of irregular growth lines. The sure and final test, however, is the optical one which consists in passing plane polarised convergent monochromatic light through a Z-cut slab (the cut faces of which have been artificially polished by smearing them with nitrobenzene or by fixing glass plates with canada-balsam) along the optic axis and examining the rings from the other side by means of an analyser. Presence of irregularities in the rings shows that the crystal is optically twinned. A photograph of rings obtained with a good crystal is shown in Fig. 3.

Electrical twinning is due to the rotation of the structure through 180° about the Z-axis in successive layers of the same specimen. This really means that the crystal has got zones having no obvious crystallographic orientation. This results under stress, in the generation of free electrical

charges of opposite signs which neutralize each other wholly or partially and thus reduce the piezo-electric efficiency of the crystal. This is detected by etching with concentrated hydrofluoric acid. Twinned regions are revealed by irregular patches of heavier corrosion and curvilinear triangular pits.

The presence of clouds, cracks, bubbles, etc., is detected visually by placing the crystal in a beaker containing nitrobenzene or a solution of 80 per cent. ethyl cinnamate and 20 per cent. xylol by volume.

Cutting

In the case of a rough specimen, the various axes have to be determined before proceeding with the cutting. There are optical as well as X-ray methods to find these out and need not be described here. We shall only illustrate the method with a more or less well-developed crystal. The crystal is so fixed on the cutting machine that the plane of the cutting disc is perpendicular to the Z-axis and then it is first cut roughly into Z-cut or primary slabs as shown in Fig. 4.

The blanks are now tested for twinning and the perpendicularity of the cut surfaces to the optical axis. The methods for the former have already been described in the previous section while the latter is tested by means of

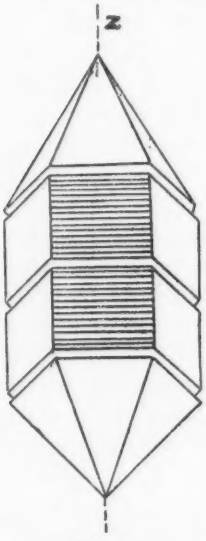


FIG. 4
Ideal crystal showing blanks cutting

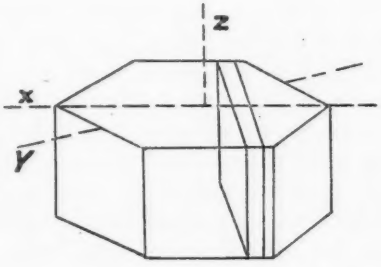


FIG. 5
X-cut Crystal

a polariscope arrangement similar to the one described for optical twinning. Here the rings observed through the analyser will wobble during the rotation of the crystal about a vertical axis if the cut surfaces are not perpendicular to the optic axis. If this happens the axis of rotation is tilted till the wobbling disappears during rotation. The ends are then cut again and the slab re-examined.

Once it has been ascertained that the blank is reasonably free from defects, it is so aligned in the cutting machine that the cutting disc passes in a plane perpendicular to one of the X-axes and thus by successive cuts a suitable X-cut cyrstal, as marked in Fig. 5 is prepared. The cutting machine is described in the following section and is shown in Fig. 6.

The Cutting Machine

It consists of a detachable copper disc (1) Fig. 6 and a wooden pulley (2) mounted on a common axle rotated by another pulley (3) fixed on the rotor shaft of a fractional horse power motor. The motor is fixed to an iron base plate (4) having a slit (5) through which it is further fixed to a wooden base. The slit provides for an easy arrangement of tightening the belt. The motor is slowed down by means of a resistance to give a linear speed of about 150 ft. per second to the edge of the cutting disc (1). This disc rotates in a gaping mouthed mud container. A strip projects from the back portion of the container almost up to the edge of the copper disc to prevent the mud splash raised by the disc, from falling outside the container.

A crystal desired to be cut is fixed between an iron plate (7) having a slit in its middle and a wooden piece (8), the arrangement being tightened by means of two bolts. If due to the shape of the crystal it is not possible to hold it in a proper plane, it is first mounted in plaster of paris and then fixed on the cutting machine. Below the slit in the iron plate (7) is fixed a catch which allows the mud to pass up only along the edge of the disc and not along its sides to guard against uneven cutting. An axle rod (9) is rivetted to the underside of the plate (7) a few inches away from the other end. It is at right angles to the slit and is held by two vertical iron plate pieces (10) fixed on a vertical plank (11) at such a height that the iron plate (7) slopes down upon the cutting disc (1). Care has been taken in mounting the axle holders (10) to keep the plane of the plate (7) at right angles to the surface of the disc (1). A guard is provided in between the cutting disc and the bearings of its axle to prevent the emery mud from falling on the bearings.

As the disc rotates through the mud-emery powder and water, its edge becomes charged with emery particles. These rub against the crystal, which

is kept pressed against the cutting edge, and a cut is automatically effected through the crystal. The speed of the cutting disc should be maintained constant to obtain a well-cut surface.

Grinding

After a crystal has been suitably cut, its surfaces have now to be ground. An arrangement, developed in the laboratory to do this work, is described below and is shown in Fig. 7.

The Grinding Machine

It consists of a cast iron disc (1), Fig. 7, mounted on the tapered upper end of an axle (2) rotating in two bearing bushes (3) fixed to the top and bottom planks of the machine. The disc (1) is rotated by means of a pulley arrangement from a fractional H. P. motor. Another pulley system (4), consisting of six pulleys, transmits motion to the crystal holder (5) and keeps it rotating simultaneously with the disc (1), though at a slower speed, to avoid unequal grinding along the radius of the disc due to variation in the linear velocity along this direction. The holder (5) is above the disc (1) and at the lower end of a vertical axle (6) rotating in two bushes (7) fixed to a wooden frame. It is an inverted L-shaped brass block (5), having all of its thickness and flat faces at right angles to each other and the upper face perpendicular to the axle. For keeping the crystal faces in appropriate positions, two guides are put in; one is a brass straight edge fixed to the vertical face of the inverted L-shaped brass block vertically, while the other is a sliding one fixed horizontally to the same block. To fill up the space a wooden cuboid (8) is placed above the crystal. Crystals are fixed between the vertical portion of the brass block and a flat wooden piece (9) by means of two bolts.

A set of four bolts fixed to a frame (10) and touching the upper bush of the crystal holder axle is put in for adjusting the perpendicularity of the axle to the surface of the grinding disc.

A metal collar (11) is fixed along the rim of the disc to keep the emery mud on the surface of the disc; and as the mud collects near the outer rim of the disc on account of the centrifugal force, a metal strip (12) ending in a rubber flap is hung loosely, as shown in the figure, so that the mud strikes against it and is thrown back towards the central region of the disc.

As the crystal holder axle is floating, its own weight keeps the crystal pressed against the surface of the disc which is kept charged with emery mud. A constant rubbing of the crystal against emery particles produces the desired surface.

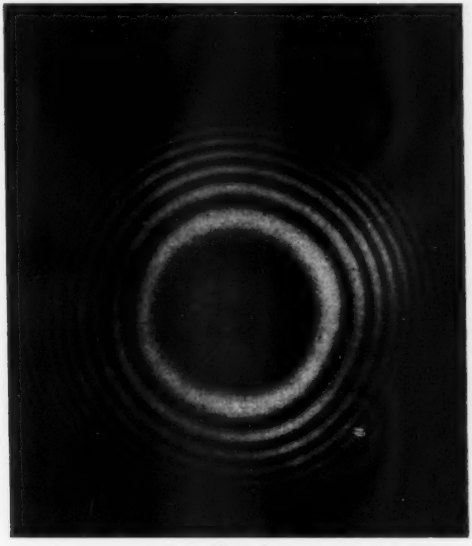


FIG. 3

Regular interference rings showing absence of optical twinning

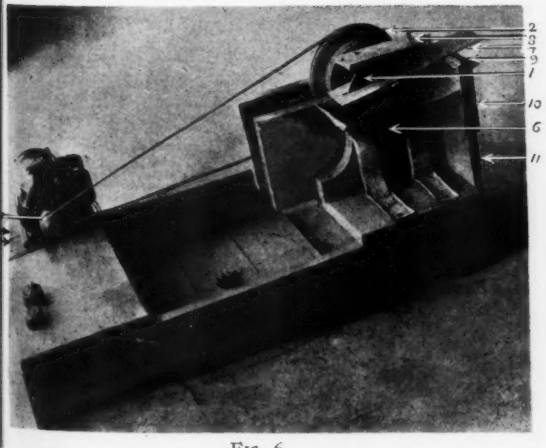


FIG. 6

Crystal cutting machine

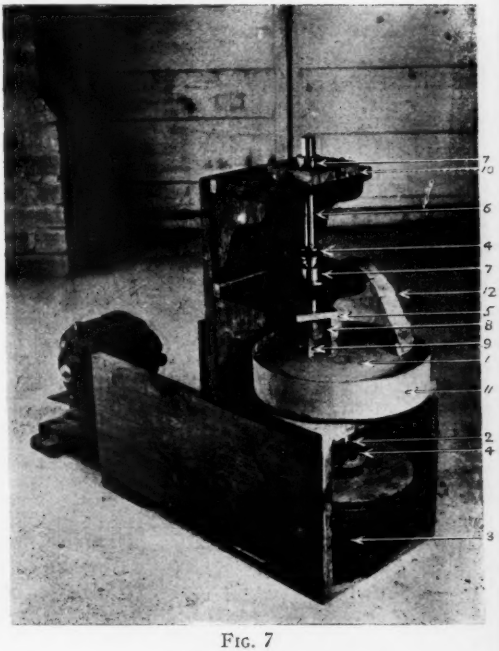


FIG. 7

Crystal grinding machine

The preparation of such cystals is of scientific and technical importance. The method developed and described above works automatically and it was thought that the publication of the technique, though it is only one stage in the solution of our problem, would be of considerable use to workers in the field.

Our thanks are due to Dr. E. McKenzie Taylor for his keen interest in the work.

PYRILIUM SALTS DERIVED FROM 4-O-METHYL RESORCYLIC ALDEHYDE

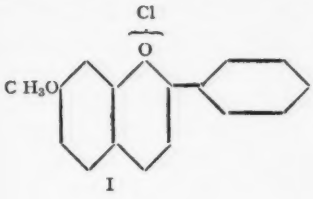
By L. Ramachandra Row and T. R. Seshadri
(*From the Department of Chemistry, Andhra University, Waltair*)

Received March, 31, 1941

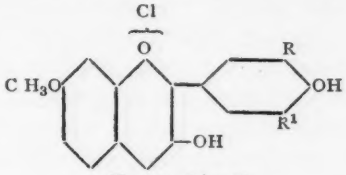
All the naturally occurring anthocyanins were originally considered to be glycosides of three fundamental anthocyanidins, (1) Pelargonidin, (2) Cyanidin and (3) Delphinidin and of certain methyl ethers of (2) and (3) namely Peonidin, Petunidin, Malvidin and Hirsutidin. These are related to the series of flavonols, Kæmferol, Quercetin and Myricetin and the benzo-pyrone part is derived from phloroglucinol. More recent work in this line mainly carried out by Robinson and collaborators has revealed the existence of other possible types, though they may not be so abundant. The flavone type is represented by Gesnerin[1] from *Gesnera fulgens* and Carajurin[2] from Chica Red. Again tetra-hydroxy benzene nucleus seems to replace the phloroglucinol nucleus in some cases.[3] In one of the most interesting group of anthocyanins, the betanin group, which seems to occur more widely than was realised before, nitrogen is found to be present.[4] The resorcinol nucleus is not uncommon amongst naturally occurring compounds of the benzo-pyrone group. Fisetin, daidzein, formonetin, butin, ψ-baptigenin, equol, umbelliferone, psoralen, and isopsoralen, karanjin, rotenone and its allies may be mentioned as some of the most important of the list. It is possible that this nucleus also finds representation amongst the anthocyanins and a number of reso-anthocyanins have been synthetically obtained by Robinson and his co-workers.[5]

In the course of an investigation on the chemical components of the roots of *Decalepis Hamiltonii*,[6] considerable amount of 4–O–methyl resorcylic aldehyde was obtained. Further certain resinous and gummy fractions appeared to contain leuco-anthocyanins exhibiting all the well recognised reactions. This aldehyde is found to be widely distributed in nature as the odoriferous principle of various plants and has been isolated in bulk from the roots of *Chlorocodon*,[7] *Decalepis Hamiltonii*,[8] *Hemidesmus Indicus*,[9] *Hanghomia Marseillei* and from the bark of *Periploca græca*.[10] Its wide occurrence suggests the possibility of related anthocyanins or leuco-anthocyanins being discovered in plant materials. It was, therefore, considered to be of interest to prepare pyrilium salts of the anthocyanidin type derived from this aldehyde and record their properties.

For purposes of this investigation, 4-O-methyl resorcylic aldehyde obtained from the roots of *Decalepis Hamiltonii* was employed. This was found to be a convenient source though this aldehyde could also be obtained by synthetic methods.[11] It was condensed with (1) acetophenone, (2) ω: 4-dihydroxy-acetophenone, (3) ω: 3: 4-triacetoxy-acetophenone and (4) ω: 3: 4: 5-tetra-acetoxy-acetophenone adopting well known methods developed by Robinson *et al.* The pyrilium salts (I), (II), (III) and (IV) were



I



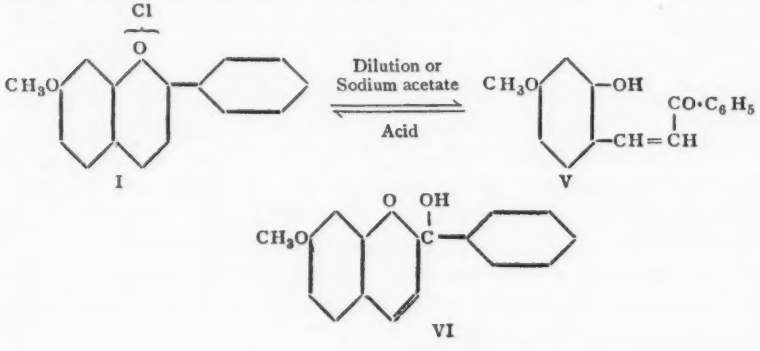
II R = R′ = H
III R = OH, R′ = H
IV R = R′ = OH

obtained in very good yields and they were readily crystallised. Though (I) was prepared by Perkin, Robinson and Turner,[12] a detailed description of its properties is not available and hence an account of it is included in this paper. All the four compounds exhibit strong greenish fluorescence in solution in concentrated sulphuric acid; but on the addition of water the fluorescence persists only in the first two cases, and the appearance of an aqueous solution of (II) exhibits close resemblance to that of an alkaline solution of fluorescein.

In regard to their extractability by amyl alcohol and "Cyanidin Reagent", stability towards the oxidation test and colour reactions with ferric chloride and alkali, compounds (II), (III) and (IV) in general resemble the corresponding anthocyanidin chlorides, pelargonidin, cyanidin and delphinidin. But they exhibit a marked poverty of tinctorial properties when examined with buffer solutions of different pH. This may be attributed to the existence of a methoxyl in the 7-position in place of a hydroxyl and not probably so much to the absence of the 5-hydroxyl. They behave normally in forming pseudo and colour bases.

A solution of compound (I) does not undergo decolorisation on dilution with alcohol or water. In this respect it agrees with other pyrilium salts which do not contain a hydroxyl in the 3-position and consequently do not easily form the ψ-base. However, on the addition of sodium acetate to a solution of the chloride in dilute hydrochloric acid, a coloured crystalline precipitate is obtained which has the semblance of a colour base. But compound (I) cannot form a colour base since it has no hydroxyl group. On

close study the precipitate turned out to be the corresponding chalkone (V) obtained by the opening out of the pyrilium ring and the identity was established by comparison with a synthetic sample of the chalkone which was prepared by condensing the aldehyde and acetophenone in the presence of alkali. This phenomenon does not seem to have been recorded before. According to Decker and Becker,[13] the corresponding pyranols are produced on pouring acetic acid solutions of such pyrilium salts into large volumes of water. On the further addition of sodium hydroxide the chalkones are generated. The individuality of these two series of isomeric compounds does not seem to have been established rigidly. In the present example sodium acetate produced a solid which was found to be identical with the synthetic chalkone, thus showing that even under these mild conditions, fission of the ring took place. Further on pouring an acetic acid solution of the pyrilium salt into a large volume of water a crystalline solid was obtained which was again found to be identical with the chalkone. No pyranol (VI) of the type mentioned by Decker and Becker could be isolated. Obviously the pyrilium ring in this type of compounds is quite readily broken up. All the three samples of the chalkone gave evidence of rapid formation of the pyrilium salt on treatment with alcoholic hydrochloric acid. Not only the production of the orange yellow colour, but also the formation of the characteristic fluorescence were quite rapid.



Experimental

7-Methoxy-3: 4'-dihydroxy-2-phenyl-benzopyrilium chloride (II).—4-O-Methyl-resorcylic aldehyde (0·25 g.) and ω: 4-dihydroxy-acetophenone (0·25 g.) were dissolved in anhydrous ethyl acetate (about 100 c.c.) and saturated in the cold with dry hydrogen chloride gas. In a few minutes the solution became orange red in colour with a strong green fluorescence and within a few hours shining red crystals began to separate. After about five

hours, the flask was left in the ice-chest to remain for two days. The contents of the flask were then filtered and the shining red crystalline mass collected. When the filtrate was treated with dry ether (3–4 volumes), only a small quantity of the anthocyanidin chloride could be further isolated. The total yield was 80%. The substance could be crystallised from 1% hydrochloric acid or from 2% methyl alcoholic hydrogen chloride. For purposes of analysis, it was crystallised from the latter when it was obtained in the form of shining red hexagonal prisms melting at 250–51°. (Found: C, 63·2; H, 4·0; OCH_3, 10·0; $C_{16}H_{13}O_3Cl$ requires C, 63·1, H, 4·2 and OCH_3, 10·2%.)

7-Methoxy-3 : 3′ : 4′-trihydroxy-2-phenyl-benzopyrilium chloride (III) was obtained by condensing 4-O-methyl-resorcylic aldehyde with ω : 3 : 4-tri-acetoxy-acetophenone[15] in a mixture of anhydrous ethyl acetate and ethyl alcohol in equal proportions by means of dry hydrogen chloride according to the method of Bradley, Robinson and Schwarzenbach.[16] At the end of two days the dark red pyrilium salt (yield 85%) was collected from the reaction mixture and crystallised from 1% hydrochloric acid. The pure substance had the form of rectangular plates exhibiting in mass a dark purplish green reflex. It was also obtained crystalline with ease by dissolving it in 1% methyl alcoholic hydrogen chloride and subsequently saturating the solution with dry hydrogen chloride. On allowing the solution to stand in an ice-chest for about 48 hours a light brownish red shining powder possessing a light green reflex settled down. Under the microscope it appeared as groups of spear heads; m.p. 258–60° (decomp.). (Found: C, 58·5, H, 4·4, OCH_3, 8·9; $C_{16}H_{13}O_4Cl$, $\frac{1}{2}H_2O$ requires C, 58·3, H, 4·2 and OCH_3, 9·4%.)

7-Methoxy-3 : 3′ : 4′ : 5′-tetra-hydroxy-2-phenyl-benzo-pyrilium chloride (*IV*).—This was obtained by condensing, as in the previous case, 4-O-methyl-resorcylic aldehyde with ω : 3 : 4 : 5-tetra-acetoxy-acetophenone[16] in a mixture of anhydrous ethyl acetate and ethyl alcohol by means of dry hydrogen chloride. A dark red powder (yield 73%) with a dull green reflex was obtained. It was purified by dissolving it in 2% methyl alcoholic hydrogen chloride and then treating the solution with a few drops of concentrated hydrochloric acid. A micro-crystalline powder separated out which showed no tendency to melt even at 340°. It could also be obtained in the form of rectangular plates with a bluish green reflex by crystallisation from dilute hydrochloric acid. (Found: C, 47·3; H, 5·4; OCH_3, 7·3; $C_{16}H_{13}O_5Cl$, $4H_2O$ requires C, 47·0; H, 5·1 and OCH_3, 7·6%.)

7-Methoxy-2-phenyl-benzopyrilium chloride (*I*) was prepared by condensing 4-O-methylresorcylic aldehyde and dry acetophenone in anhydrous ethyl acetate with dry hydrogen chloride (Perkin, Robinson and Turner, *loc. cit.*).

The yellow crystalline mass that was produced rapidly was filtered and washed with ether. The substance (yield 83%) changed, on exposure to light, from yellow to dull brown. It was sparingly soluble in dilute hydrochloric acid in the cold but dissolved freely in the hot acid. On cooling the solution it crystallised as chocolate coloured, shining, prismatic needles melting at 105–06°. (Found: C, 66·3; H, 5·5; OCH_3, 10·6; $C_{16}H_{13}O_2Cl$, H_2O requires C, 66·1; H, 5·2 and OCH_3, 10·7%.) On the addition of solid sodium acetate in the cold to a fairly strong solution of the pyrilium chloride in dilute hydrochloric acid, a milky white suspension was immediately formed which in the course of a few minutes changed to greenish blue. On leaving it aside for about three to four days, light green shining needles separated out. It was filtered and washed with water. The dry sample melted at 126–28° (decomp.). An alcoholic solution of the substance showed rapid formation of the pyrilium salt on treatment with concentrated hydrochloric acid in the cold. A mixed melting point determination with the synthetic chalkone (see below) did not show any depression.

A solution of the pyrilium chloride (0·1 g.) in glacial acetic acid (1 c.c.) was added to a large volume of water (250 c.c.). At first the solution was clear exhibiting the characteristic green fluorescence but in a few minutes it became turbid. After 24 hours the precipitated solid was filtered. Shining light green needle-shaped crystals were obtained which melted at 126–28° and showed no depression in melting point when mixed either with the synthetic chalkone or with that obtained from the pyrilium chloride on treatment with sodium acetate. The formation of the pyrilium chloride from this sample was also noticed even in the cold on the addition of concentrated hydrochloric acid. (Found: C, 75·5; H, 5·5; OCH_3, 12·0; $C_{16}H_{14}O_3$ requires C 75·6, H 5·5 and OCH_3 12·5%.)

Phenyl-4-methoxy-2-hydroxy-styrylketone.—A solution of 4-O-methyl resorcylic aldehyde (0·4 g.), acetophenone (0·4 g.) and potassium hydroxide (2 g.) in methyl alcohol (50 c.c.) was refluxed for about three hours. The deep red solution was added to water rendered acidic by the addition of hydrochloric acid, whereby the unsaturated ketone separated out as a fine yellow powder. It crystallised from aqueous alcohol in the form of yellow rectangular needles melting at 126–28°. (Found: C, 75·5; H, 5·9: OCH_3, 12·1: $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5 and OCH_3, 12·5%.) The yellow alcoholic solution of the chalkone on treatment with a few drops of concentrated hydrochloric acid turned orange red and exhibited the characteristic green fluorescence on dilution with water.

The following table gives a summary of the reactions given by the above anthocyanidin chlorides.

	I	II	III	IV
1. 1% HCl	Yellow, bright green fluorescence.	Bright orange red, no fluorescence.	Dark red with a violet tinge, no fluorescence.	Deep violet, no fluorescence.
2. Alcohol	Orange red, no fluorescence, stable and colour is not lost on standing or dilution.	Bright orange red, green fluorescence, lost on standing or dilution.	Dark crimson red, lost on standing or dilution, no fluorescence.	Dark reddish violet, lost on standing or dilution, no fluorescence.
3. Concentrated H_2SO_4	Deep green fluorescence unaffected by dilution.	Bright green fluorescence resembling alkaline solutions of fluorescein, not affected by dilution.	Weak green fluorescence destroyed by dilution.	Slight green fluorescence destroyed by dilution.
4. Extractability with Cyanidin Reagent[17]	Complete.	Complete.	Only partially extracted.	Very slight extraction.
5. Colour base formation.	Light green precipitate of chalkone.	Orange brown colour base.	Blue colour base.	Blue colour base.
6. Ferric reaction.[17]	Negative.	Negative.	Bright blue.	Bright blue.
7. Oxidation Test.[17]	Not stable.	Fairly stable.	Not quite stable.	Not stable.

Colour Reactions

The colour reactions of the anthocyanidin chlorides have been studied with a range of buffered solutions and a few others and the results recorded below. Since small changes in pH did not have any marked effect, differences of 1·2 in pH have been adopted between successive solutions (*cf.* Robertson and Robinson[18]). The nature of the various solutions is given below: (1) 1% HCl, (2) 20% HCl, (3) pH 3·2, (4) pH 4·4, (5) pH 5·6, (6) pH 6·8, (7) pH 8·0, (8) pH 9·2, (9) pH 10·4, (10) pH 11·6, (11) pH 12·8, (12) sodium acetate, (13) $NaHCO_3$, (14) Na_2CO_3 and (15) NaOH. All the buffer solutions were prepared from the B.D.H. Universal Buffer Mixture.

The anthocyanidin chloride solution was prepared by dissolving the pure substances (25·0 mg.) in absolute alcohol (100 c.c.) in a measuring flask and 1 c.c. of the solution added from a burette to 10 c.c. of the buffered solutions or of the other solutions mentioned above.

7-*Methoxy*-2-*phenyl-benzo-pyrilium chloride*.—The solution is stable and coloured deep red. (1) Pale orange red; (2) orange red; brighter than in the previous case; (3) pale orange red slightly fluorescent; (4) pale orange red; (5), (6) and (7) from pale blue to blue; (8) and (9) immediately yellow; (10) and (11) yellowish green; (12) blue; (13) dirty greenish blue; (14) greensih yellow; (15) immediately yellow. *After* 10 *minutes*: (1) to (4) orange red to pale red; (5) to (7) pale blue to blue; (8) and (9) yellow; (10) and (11) greenish yellow; (12) and (13) pale blue; (14) and (15) pale yellow to yellow. *After* 30 *minutes*: (1) to (4) no change; (5) to (7) pale blue to blue; (8) to (11) increasing intensity of yellow; (12) and (13) pale blue; (14) and (15) yellow. *After* 24 *hours*: (1) and (2) orange red; (3) very pale red; (4) almost colourless; (5) and (6) pale blue; (7) greenish yellow; (8) to (11) yellow; (12) pale blue; (13) to (15) yellow.

7-*Methoxy*-3: 4′-*dihydroxy*-2-*phenyl-benzo-pyrilium chloride*.–The solution at first was purple in colour which soon faded to yellow exhibiting a fine green fluorescence. (1) Very pale red, no marked fluorescence; (2) red solution with green fluorescence; (3) just as (1); (4) to (7) almost colourless, only a very faint red; (8) pale reddish violet; (9) violet red; (10) and (11) violet red, fading rapidly; (12) and (13) colourless at first but slowly reddish violet; (14) violet red; (15) immediately yellow. *After* 10 *minutes*: (1) almost colourless and turbid; (2) pale yellow with a pale green fluorescence; (3) to (6) pale. yellow to pale reddish brown; (7) to (9) violet red; (10) pale yellowish brown; (11) pale violet red; (12) bright reddish violet; (13) almost colourless; (14) pale yellowish brown; (15) pale yellow. *After* 30 *minutes*: (1) colourless and turbid; (2) pale yellow; (3) to (5) almost colourless; (6) very pale red;

(7) and (8) violet red; (9) to (11) pale yellow; (12) bright reddish violet; (13) to (15) pale yellow. *After* 24 *hours*: (1) almost colourless, but turbid; (2) orange red; (3) to (11) pale yellow to yellow; (12) very pale yellow; (13) to (15) yellow.

7-Methoxy-3: 3': 4'-trihydroxy-2-phenyl-benzo-pyrilium chloride.—The solution was originally deep purple, but in the course of a few minutes changed to a pale yellow colour. (1) and (2) bright red; (3) very pale red; (4) violet rapidly fading to pale violet; (5) to (8) almost colourless after shaking; (9) to (11) weak blue fading rapidly in the last case; (12) to (14) pale blue; (15) immediately pale yellow. *After* 10 *minutes*: (1) to (3) keep colour; (4) to (9) colourless to pale blue; (10) and (11) pale yellow; (12) and (13) pale blue; (14) and (15) pale yellow. *After* 30 *minutes*: (1) to (3) keep colour; (4) to (7) increasing intensity of blue; (8) to (11) from pale yellow to yellow; (12) and (13) blue; (14) and (15) yellow; *After* 24 *hours*: (1), and (2) keep the bright red colour; (3) pale violet; (4) almost colourless; (5) and (6) pale blue; (7) to (11) yellow; (12) pale blue; a slight blue precipitate collected at the bottom probably because of colour base formation; (13) to (15) pale yellow to yellow.

7-Methoxy-3: 3': 4': 5'-tetra-hydroxy-2-phenyl-benzopyrilium chloride—The solution is deep purple in colour and a slight change in intensity has only been noticed during the course of the study of colour reactions. (1) and (2) bright red; (3) violet red rapidly fades away to pale violet red; (4) to (7) at first deep violet, but rapidly fade to pale violet; (8) violet-blue, slowly fading; (9) deep blue; (10) and (11) at first deep blue, but fade away to pale brown; (12) and (13) deep pure blue; (14) blue at first, soon changes to yellowish brown; (15) immediately brown. *After* 10 *minutes*: (1) and (2) keep colour; (3) pale violet red; (4) pale reddish blue; (5) pale violet blue; (6) and (7) violet; (8) and (9) pale blue; (10) and (11) pale yellow; (12) and (13) blue; (14) and (15) pale yellow. *After* 30 *minutes*: (1) and (2) keep colour; (3) pale violet red; (4) to (7) from pale violet blue to pale violet; (8) pale blue; (9) to (11) yellow; (12) and (13) blue; (14) and (15) yellow. *After* 24 *hours*: (1) and (2) keep the colour; in both cases a red precipitate settled at the bottom; (3) and (4) almost colourless; a violet blue precipitate settled at the bottom; (5) and (6) only a pale blue colour; (7) to (11) pale yellow to yellow; (12) almost colourless, a blue precipitate at the bottom; (13) pale yellow, a bluish brown precipitate at the bottom; (14) pale yellow; (15) yellow.

Our thanks are due to Mr. G. V. L. Narasimha Murty for micro-analysis.

Summary

4-O-methyl ether of resorcylic aldehyde has been condensed with (I) acetophenone, (II) ω: 4-dihydroxy acetophenone, (III) ω: 3: 4-triacetoxy- and (IV) ω: 3: 4: 5 tetra-acetoxy-acetophenone to form pyrilium salts. Their properties and reactions are described. The first compound which has no hydroxyl groups in it undergoes change into the corresponding chalkone when its solution is treated with sodium acetate or when largely diluted with water. The reverse reaction takes place also rapidly in acid solution. The other compounds resemble closely pelargonidin, cyanidin and delphinidin though they exhibit a comparatively marked poverty of colour in solutions.

REFERENCES

(1) Robinson and Robinson .. *Biochem. Jour.*, 1932, **26**, 1649.
(2) Chapman, Perkin and Robinson *J.C.S.*, 1927, 3015.
(3) Price, Sturgess, Robinson and Robinson *Nature*, 1938, **142**, 356.
(4) Robinson, *et al.* .. *J.C.S.*, 1932, 1439; 1933, 25; 1937, 446–453.
(5) Grove, Levy, Nair and Robinson *Ibid.*, 1934, 1614.
(6) Murti and Seshadri .. *Proc. Ind. Acad. Sci.* (A), 1941, **13**, 221.
(7) Goulding and Pelly .. *Chem. Abst.*, 1908, **2**, 1708.
(8) Srinivasa Rao and Sesha Iyengar "Perfumary Essential Oil Record," 1923, **14**, 300 (*Cf.*, *Chem. Abst.*, 1923, **17**, 3490).
(9) Dutta, Ghosh and Chopra *Arch. Pharm.*, 1938, **276**, 333.
(10) Solacolu, Mavrodin and Herrmann *J. Pharm. Chim.*, 1935, **22**, 548.
(11) Ott and Nauen .. *Ber.*, 1922, **55**, 920.
(12) Perkin, Robinson and Turner *J.C.S. Trans.*, 1908, **93**, 1098.
(13) Decker and Becker .. *Ber.*, 1922, **55**, 375.
(14) Leon, Robertson, Robinson and Seshadri *J.C.S.*, 1931, 2672.
(15) Voswinkel .. *Ber.*, 1909, **49**, 4651.
(16) Bradley, Robinson and Schwarzenbach *J.S.C.*, 1930, 793.
(17) Robinson and Robinson .. *Biochem. Jour.*, 1931, 1687.
(18) Robertson and Robinson *Ibid.*, 1929, 35.

SOME IDIOSYNCRATIC NUMBERS OF RAMANUJAN

By Hansraj Gupta

(From the Department of Mathematics, Government College, Hoshiarpur)

Received March 3, 1941

(Communicated by Dr. B. L. Bhatia, D.Sc., F.N.I.)

1. Ramanujan[1] considered the ternary quadratic form:

$$x^2 + y^2 + 10\,z^2, \tag{1}$$

and stated that the odd numbers:

3, 7, 21, 31, 33, 43, 67, 79, 87, 133, 217, 219, 223, 253, 307, 391,..... cannot be expressed in the above form.

It was believed that Ramanujan's list was complete, though the dots after 391 indicated otherwise. I now find that 679 and 2719 are the only other odd numbers below 20000, which are not expressible in the said form.

In this connection, I obtained[2] for $N_2(n)$—the number of non-negative integers not exceeding n, which can be expressed in the form:

$$x^2 + y^2, \tag{2}$$

where x and y are any integers zero not excluded;—

the approximate formula[3]:

$$N_2(n) \doteqdot (\cdot 764 + \cdot 52\, n^{-\frac{9}{40}})\, n\, (\log n)^{-\frac{1}{2}} + 212 \text{ vers } (n\pi/90000), \tag{3}$$

true for all values of $n \geqslant 2$.

For values of n up to 20000, the last term in (3), *viz.*,

$$212 \text{ vers } (n\pi/90000) \doteqdot \tfrac{1}{8}\,(n/1000)^2. \tag{4}$$

For large values of n, (3) reduces to the well-known asymptotic formula:

$$N_2(n) \sim b\, n\, (\log n)^{-\frac{1}{2}}, \text{ where } b = \cdot 764.... \tag{5}$$

due to Ramanujan and Landau.

2. The following table gives the correct value of $N_2(n)$ and the approximation obtained from (3). It is note worthy that the difference between the two does not exceed six for values of n up to 20000.

n	$N_2(n)$	$N_2(n)$ by (3)
4	4	3·9
100	44	44·2
1000	331	332·6
2000	620	623·0
3000	900	901·0
4000	1172	1175·0
5000	1444	1443·1
6000	1708	1708·2
7000	1971	1970·8
8000	2231	2230·9
9000	2492	2489·3
10000	2750	2746·0
11000	3002	3001·4
12000	3254	3255·7
13000	3512	3508·9
14000	3764	3761·7
15000	4014	4013·4
16000	4262	4264·1
17000	4509	4514·2
18000	4761	4763·7
19000	5007	5012·1
20000	5259	5261·1

REFERENCES

1. Ramanujan, *Collected Papers*, 171–2.
2. *Cf.* Tricomi, *Atti. Acad. Sci. Torino.*, 1939, **74**, 369–80.
3. This form was suggested by a graph which Mr. Somdatt Chopra prepared for me.

SOME RELATIONS BETWEEN BESSEL FUNCTIONS OF THIRD ORDER AND CONFLUENT HYPERGEOMETRIC FUNCTIONS

By N. A. Shastri

(College of Science, Nagpur)

Received January 23, 1941

(Communicated by Prof. B. S. Madhava Rao)

In a recent paper[1] Varma has obtained an infinite series involving the product of Bessel functions and generalized Laguerre Polynomials. The object of the present paper is to obtain more general results and new relations involving confluent hypergeometric functions and Lommel functions.

I. In the relation

$$(yt)^{-\frac{1}{2}\alpha}\, J_\alpha\,(2\sqrt{y\,t}) = \sum_{n=0}^{\infty} \frac{t^n\, e^{-t}}{\Gamma(\alpha+n+1)}\, L_n^\alpha\,(y) \qquad (1)$$

replace $\sqrt{t}$ by $-\frac{1}{\sqrt{p}}$ and then multiply both sides of the result by $\left(\frac{y}{p}\right)^m$, where p is the operator given by the relation $\frac{1}{p^n} \doteqdot \frac{x^n}{\Gamma(n+1)}$, $R(n) > 0$.

We will obtain

$$\left(\frac{y}{p}\right)^{m-\frac{1}{2}\alpha} J_\alpha\left(-2\sqrt{\frac{y}{p}}\right) = \sum_{n=0}^{\infty} \frac{p^{-(n+m)}\, e^{-\frac{1}{p}}}{\Gamma(\alpha+n+1)}\, y^m\, L_n^\alpha\,(y) \qquad (2)$$

But[2]

$$p^{-m+\frac{\alpha}{2}}\, J_\alpha\left(-2\sqrt{\frac{1}{p}}\right) \doteqdot x^{\frac{2m-\alpha}{3}}\, J_{m,\,\alpha}\,(3\sqrt[3]{x}).$$

Hence by a theorem of operational calculus

$$\left(\frac{y}{p}\right)^{m-\frac{\alpha}{2}} J_\alpha\left(-2\sqrt{\frac{y}{p}}\right) \doteqdot (x\,y)^{\frac{2m-\alpha}{3}}\, J_{m,\,\alpha}\,(3\sqrt[3]{xy}). \qquad (3)$$

Again[3] $$p^{-(n+m)}\, e^{-\frac{1}{p}} \doteqdot x^{\frac{1}{3}(n+m)}\, J_{n+m}\,(2\sqrt{x}). \qquad (4)$$

Using these results we can interpret the equation (2) and get after a little simplification

$$\left(\frac{\sqrt{x}}{y}\right)^{\frac{1}{3}(m-2\alpha)} \cdot J_{m,\alpha}\ (3\sqrt[3]{xy}) = \sum_{n=0}^{\infty} \frac{x^{\frac{1}{2}n}\, y^\alpha\, J_{n+m}\,(2\sqrt{x})}{\Gamma(\alpha+n+1)}\, L_n^\alpha\,(y) \qquad (5)$$

$$= \sum_{n=0}^{\infty} \frac{(-)^n \binom{-\alpha-1}{n}}{\Gamma(\alpha+n+1)}\, x^{\frac{1}{2}n}\, y^{\frac{1}{2}(\alpha-1)}\, e^{\frac{1}{2}y}\, J_{n+m}\,(2\sqrt{x})\, M_{n+\frac{\alpha+1}{2},\,\frac{\alpha}{2}}\,(y) \qquad (6)$$

using the relation

$$L_n^{\alpha}(y) = (-)^n \binom{-\alpha-1}{n} y^{-\frac{\alpha+1}{2}} e^{y/2} M_{n+\frac{\alpha+1}{2}, \frac{\alpha}{2}}(y).$$

where $M_{k,m}$ is one of Whittaker's confluent hypergeometric functions.

II. Now multiply the equation (2) by $\frac{\omega}{p^2+\omega^2}$ and $\frac{p}{p^2+\omega^2}$ respectively, we get

$$\frac{1}{p} \cdot \frac{p\omega}{(p^2+\omega^2)} \left(\frac{y}{p}\right)^{m-\frac{1}{2}\alpha} J_{\alpha}\left(-2\sqrt{\frac{y}{p}}\right) \doteqdot \sum_{n=0}^{\infty} \frac{\omega e^{-\frac{1}{p}}}{p^{n+m}(p^2+\omega^2)} \frac{y^m L_n^{\alpha}(y)}{\Gamma(\alpha+n+1)}$$

and

$$\frac{1}{p} \cdot \frac{p^2}{(p^2+\omega^2)} \left(\frac{y}{p}\right)^{m-\frac{1}{2}\alpha} J_{\alpha}\left(-2\sqrt{\frac{y}{p}}\right) \doteqdot \sum_{n=0}^{\infty} \frac{e^{-\frac{1}{p}}}{p^{n+m-1}(p^2+\omega^2)} \frac{y^m L_n^{\alpha}(y)}{\Gamma(\alpha+n+1)}.$$

We now interpret these results with the help of the product theorem of the operational calculus, the relation (3) and

$$\frac{p\omega}{p^2+\omega^2} \doteqdot \sin \omega x,$$

$$\frac{p^2}{p^2+\omega^2} \doteqdot \cos \omega x.$$

and[4] $$U_n(2\omega x, 2\sqrt{x}) \doteqdot \frac{\omega^n e^{-\frac{1}{p}}}{p^{n-2}(p^2+\omega^2)} \qquad R(n) > -1.$$

where U_n is a Lommel function. We get

$$\int_0^x \begin{matrix}\sin \\ \cos\end{matrix} [\omega(x-\xi)] \left(\frac{\xi}{\sqrt{y}}\right)^{\frac{2m-\alpha}{3}} J_{m,\alpha}(3\sqrt[3]{\xi y})\, d\xi.$$

$$= \sum_{n=0}^{\infty} \frac{y^{\frac{\alpha}{2}} L_n^{\alpha}(y)}{\omega^{m+n+1}\Gamma(\alpha+n+1)} \frac{U_{n+m+2}}{U_{n+m+1}} [2\omega x, 2\sqrt{x}] \tag{7}$$

$$= \sum_{n=0}^{\infty} \frac{(-)^n \binom{-\alpha-1}{n} y^{-\frac{1}{2}} e^{\frac{y}{2}}}{\omega^{m+n+1}\Gamma(\alpha+n+1)} M_{n+\frac{\alpha+1}{2}, \frac{\alpha}{2}}(y) \frac{U_{m+n+2}}{U_{m+n+1}} [2\omega x, 2\sqrt{x}]. \tag{8}$$

We will now obtain the particular cases of the results obtained.

(i) If we put α equal to zero in (5) and (7) we get

$$\left(\frac{\sqrt{x}}{y}\right)^{\frac{m}{3}} J_{m,0}(3\sqrt[3]{xy}) = \sum_{n=0}^{\infty} \frac{x^{\frac{1}{2}n} J_{n+m}(2\sqrt{x})}{n!} L_n(y) \tag{9}$$

and $$\int_0^x \begin{matrix}\sin \\ \cos\end{matrix} [\omega(x-\xi)] \left(\frac{\xi^2}{y}\right)^{\frac{m}{3}} J_{m,0}(3\sqrt[3]{\xi y})\, d\xi$$

$$= \sum_{n=0}^{\infty} \frac{L_n(y)}{n!\,\omega^{n+m+1}} \frac{U_{n+m+2}}{U_{n+m+1}} [2\omega x, 2\sqrt{x}] \tag{10}$$

(ii) If we put α equal to one and use the result

$$y\, L_n^{(1)}(y) = (-)^n\,(n+1)\, e^{\frac{y}{2}}\, k_{2n+2}\left(\frac{y}{2}\right)$$

we will get the relations involving Bateman's k-functions;

$$e^{-\frac{y}{2}}\left(\frac{\sqrt{x}}{y}\right)^{\frac{m-2}{3}} J_{m,1}(3\sqrt[3]{xy}) = \sum_{n=0}^{\infty} \frac{(-\sqrt{x})^n}{n!}\, k_{2n+2}\left(\frac{y}{2}\right) J_{n+m}(2\sqrt{x}) \quad (11)$$

and $e^{-\frac{y}{2}} \int_0^x \begin{matrix}\sin\\ \cos\end{matrix} [\omega(x-\xi)] \left(\frac{\xi^2}{y}\right)^{\frac{1}{3}(m-\frac{1}{2})} J_{m,1}(3\sqrt[3]{\xi y})\, d\xi.$

$$= \sum_{n=0}^{\infty} \frac{(-)^n\, y^{-\frac{1}{2}}\, k_{2n+2}\left(\frac{y}{2}\right)}{n!\ \omega^{n+m+1}} \cdot \frac{U_{n+m+2}}{U_{n+m+1}}[2\omega x, 2\sqrt{x}] \quad (12)$$

(iii) Now put $\alpha = -\frac{1}{2}$ and use the relation

$$2^n\, n!\, L_n^{-\frac{1}{2}}(y) = (-)^n\, e^{\frac{1}{4}y}\, D_m(\sqrt{2y})$$

we get $\sqrt{\pi}\, e^{-\frac{1}{2}y}\left(\frac{\sqrt{x}}{y}\right)^{\frac{1}{3}(m+1)} J_{m,-\frac{1}{2}}(3\sqrt[3]{xy}) = \sum_{n=0}^{\infty} \frac{(-2\sqrt{x})^n\, y^{-\frac{1}{2}}}{(2n)!}$

$$J_{n+m}(2\sqrt{x})\, D_{2n}(\sqrt{2y}) \quad (13)$$

and $\sqrt{\pi}\, e^{-\frac{1}{2}y} \int_0^x \begin{matrix}\sin\\ \cos\end{matrix} [\omega(x-\xi)] \left(\frac{\xi^2}{y}\right)^{\frac{1}{3}(m+\frac{1}{2})} J_{m,-\frac{1}{2}}(3\sqrt[3]{\xi y})\, d\xi$

$$= \sum_{n=0}^{\infty} \frac{(-2)^n\, y^{-\frac{1}{2}}\, D_{2n}(\sqrt{2y})}{(2n)!\ \omega^{n+m+1}} \cdot \frac{U_{n+m+2}}{U_{n+m+1}}[2\omega x, 2\sqrt{x}] \quad (14)$$

where $D_{2n}(y)$ is a parabolic cylinder function.

(iv) Finally replace α by $\frac{1}{2}$ and use the result

$$2^{n+\frac{1}{2}}\, n!\, L_n^{\frac{1}{2}}(y) = (-)^n\, y^{-\frac{1}{2}}\, e^{\frac{1}{4}y}\, D_{2n+1}(\sqrt{2y})$$

and the duplication formula of the Gamma functions we get

$$\sqrt{\frac{\pi}{2}}\, e^{-\frac{1}{2}y}\left(\frac{\sqrt{x}}{y}\right)^{\frac{m-1}{3}} J_{m,\frac{1}{2}}(3\sqrt[3]{xy}) = \sum_{n=0}^{\infty} \frac{(-2\sqrt{x})^n}{(2n+1)!} J_{n+m}(2\sqrt{x}) \times$$

$$\times D_{m+1}(\sqrt{2y}) \quad (15)$$

and $\sqrt{\frac{\pi}{2}}\, e^{-\frac{1}{2}y} \int_0^x \begin{matrix}\sin\\ \cos\end{matrix} [\omega(x-\xi)] \left(\frac{\xi^2}{y}\right)^{\frac{1}{3}(m-\frac{1}{2})} J_{m,\frac{1}{2}}(3\sqrt[3]{\xi y})\, d\xi.$

$$= \sum_{n=0}^{\infty} \frac{(-2)^n\, y^{-\frac{1}{2}}\, D_{2n+1}(\sqrt{2y})}{(2n+1)!\ \omega^{n+m+1}} \cdot \frac{U_{n+m+2}}{U_{n+m+1}}[2\omega x, 2\sqrt{x}]. \quad (16)$$

If in (15) we put $m=\frac{1}{2}$ and use Humbert's[2] result

$$x^2\, J_{\frac{1}{2},\frac{1}{2}}(3x)=\frac{1}{2\pi}\int_0^\infty e^{-s^2/16x^3}\ \mathrm{ber}\,(2\sqrt{s})\,ds.$$

we get a relation involving Kelvin's ber function as

$$\sqrt{\frac{2}{\pi}}\,e^{-\frac{1}{2}y}\left(\frac{\sqrt{x}}{y}\right)^{\frac{1}{2}}\int_0^\infty e^{-s^2/16xy}\cdot\ \mathrm{ber}\,(2\sqrt{s})\,ds$$

$$=\sum_{n=0}^{\infty}\frac{(-2\sqrt{x})^{n+2}}{(2n+1)!}\,J_{n+\frac{1}{2}}(2\sqrt{x})\,D_{2n+1}(\sqrt{2y}) \tag{17}$$

The results obtained by Varma can be deduced as particular cases of (5) (9), (11), (13) and (15) if we replace m by zero in them.

III. The relation (2), when its left-hand side is interpreted with the help of (3), becomes

$$(xy)^{\frac{2m-\alpha}{3}}\,J_{m,\alpha}(3\sqrt[3]{xy})\doteqdot\sum_{n=0}^{\infty}\frac{p^{-(n+m)}\,e^{-\frac{1}{p}}}{\Gamma(\alpha+n+1)}\,y^m\,L_n^\alpha(y).$$

Again[5] we have

$$\frac{x^l}{\Gamma(l+1)\,2^{l+\frac{1}{2}}\left(x+\frac{1}{a}\right)^{l+\frac{1}{2}}}\doteqdot\sqrt{p}\;e^{p/2a}\,D_{-2l-1}\left(\sqrt{\frac{2p}{a}}\right)$$

$$R(l)>-\tfrac{1}{2},\ a>0.$$

We now apply to these results Parseval's theorem as used in operational calculus, we get

$$\int_0^\infty\left(\frac{x^2}{y}\right)^{\frac{1}{2}\left[m-\frac{2\alpha+3}{4}\right]}\,e^{\frac{x}{2a}}\,D_{-2l-1}\left(\sqrt{\frac{2x}{a}}\right)\,J_{m,\alpha}(3\sqrt[3]{xy})\,dx$$

$$=\sum_{n=0}^{\infty}\frac{\Gamma(n+m+\frac{1}{2})\,y^{\frac{2\alpha+1}{4}}\,a^{\frac{1}{2}(l+m+n)}}{\Gamma(l+1)\,\Gamma(\alpha+n+1)\,2^{l+\frac{1}{2}}}\,e^{\frac{1}{2}a}\,L_n^\alpha(y)\,W_{-\frac{1}{2}(l+m+n),\,\frac{1}{2}(m+n-l)}(a) \tag{18}$$

$$R(l)>-\tfrac{1}{2},\quad R(\tfrac{1}{2}+n+m)\geqslant 0\quad\text{and}\quad a>0$$

after evaluating the integral occurring on the right-hand side

$$\int_0^\infty e^{-\frac{1}{x}}\,x^{l-n-m-1}\left(x+\frac{1}{a}\right)^{-l-\frac{1}{2}}dx=\Gamma(n+m+\tfrac{1}{2})\,a^{\frac{1}{2}(l+m+n)}$$

$$e^{\frac{1}{2}(a)}\,W_{-\frac{1}{2}(l+m+n),\,\frac{1}{2}(m+n-l)}(a).$$

with the help of

$$W_{k,\,m}(z) = \frac{e^{-\frac{1}{2}z}\, z^k}{\Gamma(\frac{1}{2}-k+m)} \int_0^\infty e^{-t}\, t^{-k-\frac{1}{2}+m} \left(1+\frac{t}{z}\right)^{k-\frac{1}{2}+m} dt$$

$$R\,(k-\tfrac{1}{2}-m) < 0.$$

Proceeding as before we can obtain the following particular cases:

$$(i) \int_0^\infty \left(\frac{x^2}{y}\right)^{\frac{1}{3}\left(m-\frac{5}{4}\right)} e^{\frac{x}{2a}}\, J_{m,\,1}\,(3\sqrt[3]{xy})\, D_{-2l-1}\left(\sqrt{\frac{2x}{a}}\right) dx$$

$$= \sum_{n=0}^{\infty} \frac{(-)^n\, \Gamma(n+m+\frac{1}{2})\, y^{-\frac{1}{4}}}{n!\, \Gamma(l+1)\, 2^{l+\frac{1}{4}}}\, e^{\frac{1}{2}(y+a)}\, a^{\frac{1}{2}(l+n+m)}\, k_{2n+2}(y/2)$$

$$W_{-\frac{1}{2}(l+m+n),\,\frac{1}{2}(m+n-l)}(a) \qquad (19)$$

$$(ii) \int_0^\infty \left(\frac{x^2}{y}\right)^{\frac{1}{2}(m-\frac{1}{2})} e^{x/2a}\, J_{m,-\frac{1}{2}}\,(3\sqrt[3]{xy})\, D_{-2l-1}\left(\sqrt{\frac{2x}{a}}\right) dx$$

$$= \sum_{n=0}^{\infty} \frac{(-)^n\, \Gamma(n+m+\frac{1}{2})\, a^{\frac{1}{2}(l+m+n)}}{(2n)!\, \sqrt{\pi}\, \Gamma(l+1)\, 2^{l-n+\frac{1}{2}}} \cdot e^{\frac{1}{2}(a+y)}\, D_{2n}\,(\sqrt{2y})$$

$$W_{-\frac{1}{2}(l+m+n),\,\frac{1}{2}(m+n-l)}(a) \qquad (20)$$

and

$$(iii) \int_0^\infty \left(\frac{x^2}{y}\right)^{\frac{1}{2}(m-1)} e^{x/2a}\, J_{m,-\frac{1}{2}}\,(3\sqrt[3]{xy})\, D_{-2l-1}\left(\sqrt{\frac{2x}{a}}\right) dx$$

$$= \sum_{n=0}^{\infty} \frac{(-)^n\, \Gamma(n+m+\frac{1}{2})\, a^{\frac{1}{2}(l+m+n)}}{(2n+1)!\, \sqrt{\pi}\, \Gamma(l+1)\, 2^{l-n}}\, e^{\frac{1}{2}(a+y)}\, D_{2n+1}(\sqrt{2y})$$

$$W_{-\frac{1}{2}(l+m+n),\,\frac{1}{2}(m+n-l)}(a) \qquad (21)$$

REFERENCES

(1) Varma .. *Proc. Ind. Acad. Sci.*, 1940, **12**, 532–34.

(2) Humbert .. *Atti. Pont. Accad. delle Scienze Nov. Lync.*, Anno 87, Sess. IV, 323–31.

(3) ———— .. *Le Calcul Symbolique* (Paris), 1934.

(4) Shastri .. *Phil. Mag.* (7), 1938, **25**, 931.

(5) ———— .. *Math. Zeit.*, 1939, **44**, 790.

ON THE SUM FUNCTION CONNECTED WITH PRIMITIVE ROOTS

By S. S. Pillai

(*Travancore University*)

Received April 16, 1941

(Communicated by Prof. B. S. Madhava Rao)

§ 1. Let $P(n)$ denote the number of primitive roots of n and $\phi(x)$ Euler's ϕ function. The object of this paper is to prove the following:

Theorem I*. If $S(x) = \sum_{p \leqslant x} \phi(p-1)$, then

$$S(x) = A \cdot Li(x^2) + 0\{x^2/(\log x)^m\}, \text{ where}$$

$$A = \sum_{n=1}^{\infty} \frac{\mu(n)}{n\phi(n)} \text{ and } Li(x) = \int_2^x \frac{dt}{\log t}$$

and p is a prime.

Theorem II: If $T(x) = \sum_{n \leqslant x} P(n)$, then

$$T(x) = A\left\{Li(x^2) + Li\left(\frac{x^2}{4}\right)\right\} + 0\{x^2/(\log x)^m\}.$$

§ 2. The following further notations are used:

$$y = \log x;\ lx = \log x;\ t = \phi(d).$$

$\pi(x, d, 1)$ is the number of primes $\leqslant x$ in the arithmetic progression $md+1$, where $m = 1, 2, \cdots\cdots f(x) = \pi(x, d, 1)$.

m is a given integer.

$$x \geqslant 2m^2. \tag{1}$$

The following result is used:

Lemma 1: If $d \leqslant y^m$, then

$$f(x) = \frac{1}{t}\int_2^x \frac{dt}{\log t} + 0\,(x/y^{m+1}).$$

---

* In *Rendi. Cir. Mat. Palerms*, **57**, 1933, Titchmarsh has considered the sum $\sum_{p \leqslant x} d(p-1)$ $S(x)$ turns out to be much easier than the above sum.

This lemma is proved by Walfisz in *Math. Zeitschrift*, 40 (1936).

$$\mathrm{M} = [x/t\, y^m.] \tag{3}$$

Since $$x \geqslant 2m^2, \text{ when } d < y^m,\ d < \mathrm{M}^{m-1} \tag{4}$$

Lemma 2:

§ 3. If $\mathrm{S}_d(x) = \sum_{\substack{p = rd+1 \\ p \leqslant x}} p$, then when $d < y^m$,

$$\mathrm{S}_d(x) = \frac{1}{t}\,\mathrm{Li}(x^2) + \mathrm{O}\{x^2/(t \cdot y^m)\}$$

$$\mathrm{S}_d(x) = \sum_{n \leqslant x} n\{f(n) - f(n-1)\}$$

$$= \sum_{n=1}^{x-1} f(n)\{n - (n+1)\} + xf(x)$$

$$= xf(x) - \sum_{n=1}^{x} f(n) + \mathrm{O}(x/t)$$

$$= xf(x) - \sum_{n>\mathrm{M}}^{x} f(n) + \sum_{n=1}^{\mathrm{M}} f(n) + \mathrm{O}(x/t)$$

$$= xf(x) - \sum_{n>\mathrm{M}}^{x} \left\{ \sum_{r=1}^{m-1} \frac{n(r-1)!}{t(\ln)^r} + \mathrm{O}\left(\frac{n}{t(\ln)^m}\right)\right\} + \mathrm{O}\left(\frac{x^2}{t\, y^m}\right)$$

from (4) and lemma (1)

$$= xf(x) - \frac{1}{t}\sum_{r=1}^{m-1}(r-1)!\sum_{n>\mathrm{M}}^{x}\frac{n}{(\log n)^r} + \mathrm{O}(x^2/ty^m)$$

$$= xf(x) - \frac{1}{t}\sum_{r=1}^{m-1}(r-1)!\int_{\mathrm{M}}^{x}\frac{t\,dt}{(\log t)^r} + \mathrm{O}(x^2/ty^m)$$

$$= \frac{x^2}{t}\sum_{r=1}^{m-1}\frac{(r-1)!}{y^r} - \frac{1}{t}\sum_{r=1}^{m-1}\sum_{h=0}^{m-1-r}(r-1+h)!\, x^2/(2^{h+1}\, y^{r+h}) + \mathrm{O}(x^2/ty^m), \quad \text{(integrating by parts)}$$

$$= \frac{x^2}{t}\sum_{r=1}^{m-1}\frac{(r-1)!}{y^r} - \frac{x^2}{t}\sum_{s=1}^{m-1}\frac{(s-1)!}{y^s}\sum_{h=0}^{s-1}\frac{1}{2^{h+1}} + \mathrm{O}(x^2/ty^m)$$

$$= \frac{x^2}{t}\sum_{r=1}^{m-1}\frac{(r-1)!}{y^r}\left(1 - \frac{1}{2} - \frac{1}{2^2} - \cdots - \frac{1}{2^r}\right) + \mathrm{O}(x^2/ty^m)$$

$$= \frac{x^2}{t}\sum_{r=1}^{m-1}\frac{(r-1)!}{2^r y^r} + \mathrm{O}(x^2/ty^m)$$

$$= \frac{1}{t} \sum_{r=1}^{m-1} \frac{(r-1)!\, x^2}{(l\, x^2)^r} + O(x^2/ty^m)$$

$$= \frac{1}{t} \int_2^{x^2} \frac{dt}{\log t} + O(x^2/ty^m)$$

$$= \frac{1}{t} \operatorname{L} i(x^2) + O(x^2/ty^m).$$

§ 4. THEOREM I: $S(x) = A \cdot \operatorname{L}i(x^2) + O(x^2/y^m)$.

$$S(x) = \sum_{p \leqslant x} \phi(p-1) = \sum_{p \leqslant x} (p-1) \sum_{d/(p-1)} \frac{\mu(d)}{d}$$

$$= \sum_{d \leqslant x-1} \frac{\mu(d)}{d} \sum_{\substack{p = rd+1 \\ p \leqslant x}} (p-1)$$

$$= \sum_{d \leqslant x} \frac{\mu(d)}{d} S_d(x) + O(x)$$

$$= \sum_{d \leqslant y^m} \cdots\cdots + \sum_{d > y^m} \cdots\cdots + O(x) = S_1 + S_2 + O(x), \text{ say.}$$

From lemma (2),

$$S_1 = \sum_{d \leqslant y^m} \frac{\mu(d)}{d} \left\{ \frac{1}{t} \operatorname{L}i(x^2) + O(x^2/t\, y^m) \right\}$$

$$= \operatorname{L}i(x^2) \left\{ \sum_{d \leqslant y^m} \frac{\mu(d)}{d\, \phi(d)} \right\} + O\left(\frac{x^2}{y^m}\right) \sum \frac{1}{d\, \phi(d)}$$

$$= \operatorname{L}i(x^2) \left\{ A + O \sum_{n > y^m} \frac{1}{n\, \phi(n)} \right\} + O(x^2/y^m)$$

$$= A \cdot \operatorname{L}i(x^2) + O(x^2/y^m) \tag{5}$$

Now

$$S_2 = O\{ \sum_{d > y^m} S_d(x)/d \}$$

$$= O\left\{ \sum_{d > y^m} \frac{1}{d} \left(d + 1 + 2d + 1 + \cdots\cdots + \left[\frac{x}{d}\right] d + 1 \right) \right\}$$

$$= O \sum_{d > y^m} \frac{x^2}{d^2} = O(x^2/y^m) \tag{6}$$

From (5) and (6), the theorem follows:

§ 5. THEOREM II: $T(x) = A\{\operatorname{L}i(x^2) + \operatorname{L}i(\tfrac{1}{2} x^2)\} + O(x^2/y^m)$

We know that $P(n) = 0$, when $n \neq 2, 4, p^\lambda$, or $2p^\lambda$, where p is an odd prime.

Further, $P(2p^\lambda) = P(p^\lambda) = \phi\{\phi(p^\lambda)\}$.

Hence $T(x) = \sum_{n \leqslant x} P(n) = \sum_{p^\lambda \leqslant x} \phi\{\phi(p^\lambda)\} + \sum_{2p^\lambda \leqslant x} \phi\{\phi(p^\lambda)\} = S_1 + S_2$

$$S_1 = \sum_{p \leqslant x} \phi\{\phi(p) + O \sum_{\substack{p^\lambda \leqslant x \\ \lambda \geqslant 2}} (p-1)\, p^{\lambda-1}$$

$$= \sum_{p \leqslant x} \phi(p-1) + O(x \sqrt{x \log x})$$

$$= A\, \mathrm{L}i(x^2) + O(x^2/y^m), \text{ from Theorem I.}$$

Similarly we consider S_2.

§ 6. If $\sigma_{-1}(n) = \sum_{d|n} \frac{1}{d}$, it can be proved similarly that

$$\sum_{p \leqslant x} \sigma_{-1}(p-1) = B \cdot \mathrm{L}\, i(x^2) + O(x^2/y^m),$$

where $$B = \sum_{n=1}^{\infty} \frac{1}{n\phi(n)}.$$

ON M CONSECUTIVE INTEGERS—III*

By S. S. Pillai

(*Travancore University*)

Received April 16, 1941

(Communicated by Dr. T. Vijayaraghavan)

The object of this note is to prove

Theorem I: *When* $m \geqslant 17$, *we can find* m *consecutive integers such that no number in the set is prime to all the rest in the set.*

In Vol. 6 of the *Quarterly Journal of Mathematics*, P. Erdös' has proved that *there is a constant* c *such that we can find* $c\,p\log p/(\log\log p)^2$ *consecutive integers so that no one of them is prime to* $2\cdot 3\cdot 5\ldots p$. From this result, not only the above theorem for all large *m*, but also the following general theorem follows:

Theorem II: *When* m *is large, we can find* m *consecutive integers such that each number in the set has at least* $c\log m/(\log\log m^2)$ *numbers of the set having a common factor with it.*

In an earlier paper† I gave Theorem I as a conjecture. I owe to a letter from Dr. T. Vijayaraghavan the revival of my interest in the problem, and only after receiving his letter I noticed the above connections. The main idea of the proof of Theorem I is extracted from Erdös' paper.

Notations

$$k=[(\log m)/\log 2];\quad 1\leqslant b\leqslant m;\quad 1\leqslant i\leqslant k \tag{1}$$

The numbers $q_1, q_2, \cdots q_k, r_1, r_2, \cdots r_k$ are distinct primes, and

$$\frac{m}{4}<q_i\leqslant \tfrac{1}{2}m,\ \tfrac{1}{2}m<r_i<2q_i\ (i=1,2,\cdots k).$$

---

* *Proc. Ind. Acad. Sci.* (A), 1940, **11**, 6–12.

† From Abstract No. 405, *Bulletin of the A. M. S.*, 1940, **46**, p. 751 (September Number), we see that A. T. Brauer has proved the main result of this paper. But I got the proof in August 1940. Further in a letter to me (July 30, 1940), William R. Scott has proved the above Theorem I by an elegant method for $17\leqslant m<2,491,906,561$.

The numbers $t_1, t_2 \cdot \cdot \cdot \cdot t_l$ are all the distinct primes $\leqslant \frac{1}{2}m$, and different from 2, $q_1, q_2 \cdot \cdot \cdot \cdot q_k$. We denote as usual by $\pi(x)$ and $\theta(x)$ respectively the number of primes not exceeding x, and the sum of the logarithms of primes not exceeding x. Let $c = \cdot 345$, $d = \cdot 69$, and let $f(x)$ denote the smaller of the two numbers

$$\pi(\tfrac{1}{2}x) - \pi(cx) \text{ and } \pi(dx) - \pi(\tfrac{1}{2}x);$$

S(x) denotes $\cdot 086\, ax - 2a\sqrt{x} - 4 \cdot 5 \log^2 x - 21 \log x - 20,$

where $a = \frac{1}{2}\log 2 + \frac{1}{3}\log 3 + \frac{1}{5}\log 5 - \frac{1}{30}\log 30 > \cdot 9.$

We say that a number $y + b$ is P if for some value of z $(\neq y + b)$ from among the numbers $y+1, y+2 \cdot \cdot \cdot \cdot y+m$ we have $(y+b, z) > 1$.

Lemma 1.‡ *If* $p \leqslant \frac{1}{2}$m *and* p|(y + b) *then* y + b *is* P.

For either $y + b - p$ or $y + b + p$ is in the set of numbers $y+1, y+2, \cdot \cdot \cdot \cdot y+m$.

Lemma 2. *If* m *is such that* $q_1, q_2, \cdot \cdot \cdot \cdot q_k$ *and* $r_1, r_2, \cdot \cdot \cdot \cdot r_k$ *exist then we can determine* y *such that* y + b *is P for every* b.

We take y such that

$$y \equiv 1 \pmod 2,$$
$$y \equiv 0 \pmod{t_r} \qquad (r = 1, 2, \cdot \cdot \cdot \cdot l),$$
$$y + 2^i \equiv 0 \pmod{q_i} \qquad (i = 1, 2, \cdot \cdot \cdot \cdot k),$$
$$y + 2q_i \equiv 0 \pmod{r_i} \qquad (i = 1, 2, \cdot \cdot \cdot \cdot k).$$

If b is odd then $y + b$ is even, and then plainly $y + b$ is P. The same conclusion holds if $b = 2^i$ $(i = 1, 2, \cdot \cdot \cdot \cdot k)$ for the $q_i | (y + b)$, and $q_i \leqslant \frac{1}{2}m$. Again the same conclusion holds if $t_r | b$, for then $t_r | y + b$. If b does not come under any of the above three cases then b is even and is divisible by atleast one of the numbers $q_1, q_2, \cdot \cdot \cdot \cdot q_k$. Hence if $q_i | b$, then $b = 2q_i$, since $m/4 < q_i \leqslant \frac{1}{2}m$. It follows that $y + b = y + 2q_i$ is divisible by r_i (on account of our choice of y) and as

$$y + b - r_i = y + 2q_i - r_i\,(> y)$$

is also divisible by r_i we see that $y + b$ is P in this case also. This completes the proof of the lemma.

Lemma 3. f(m) > k *whenever* m > 12321.

‡ This is due to Dr. T. Vijayaraghavan.

From page 91 of Landau's '*Primzahlen*', we have that

$$\theta(x) > a\,x - 2\cdot4\,a\sqrt{x} - 1\cdot5\log^2 x - 13\log x - 15,$$

and $$\theta(x) < 1\cdot2\,a\,x + 3\log^2 x + 8\log x + 5.$$

Hence $$\theta(\cdot5\,m) - \theta(\cdot345\,m) > \cdot5\,am - 2\cdot4\,a\sqrt{\cdot5m} - 1\cdot5\log^2 m,$$

$$- 13\log m - 15 - \cdot414\,am - 3\log^2 m - 8\log m - 5 > \mathrm{S}(m),$$

and $$\theta(\cdot69\,m) - \theta(\cdot5\,m) > \cdot69\,am - 2\cdot4\,a\sqrt{\cdot69\,m} - 1\cdot5\log^2 m$$

$$- 13\log m - 15 - \cdot6\,a\,m - 3\log^2 m - 8\log m - 5 > \mathrm{S}(m). \quad (4)$$

Therefore, $f(m)\log m > \mathrm{S}(m)$. From this we get that $f(m) > k$, if

$\mathrm{S}(m)/\log m > \log m/\log 2$, or if $\mathrm{S}(m) > 1\cdot5\log^2 m$, or if

$$a(\cdot086\,m - 2\sqrt{m}) > 6\log^2 m + 21\log m + 20 \quad (5)$$

If $m = 12321$, then $6\log^2 m + 21\log m + 20 < 751$, and

$$a(\cdot086\,m - 2\sqrt{m}) > \cdot9 \times 837\cdot6 > 753.$$

Further $\mathrm{S}(m) - 1\cdot5\log^2 m$ is an increasing function of m when $m \geqslant 12321$.

Hence if $m \geqslant 12321$ then (5) is satisfied, and therefore $f(m) > k$.

Lemma 4. *When* $\mathrm{m} \geqslant 12321$, *Theorem I is true.*

Every prime in the interval $(\cdot5\,m,\ \cdot69\,m)$ is less than twice any prime in $(\cdot345\,m,\ \cdot5\,m)$. So, by lemma (3), $q_1,\ q_2 \cdot\cdot\cdot\cdot q_k$ and $r_1, r_2, \cdot\cdot\cdot r_k$ exist. Therefore, from lemma (2), the present one follows:

Lemma 5. *When* $17 \leqslant \mathrm{m} \leqslant 430$, *Theorem I is true.* This is verified in my paper referred to above.

Lemma 6. *When* $422 \leqslant \mathrm{m} \leqslant 12335$, *Theorem I is true.*

The tables at the end give sufficient number of q_i and r_i. Hence the lemma follows from lemma (3).

Theorem I follows from lemmas (4), (5) and (6).

Table for q_i *and* r_i

$422 \leqslant m \leqslant 660$ $k=8$ or 9		$635 \leqslant m \leqslant 1045$ $k=9$ or 10		$1043 \leqslant m \leqslant 1821$ $k=10$	
q_i	r_i	q_i	r_i	q_i	r_i
167	331	269	523	461	911
173	337	271	541	463	919
179	353	277	547	467	929
181	359	281	557	479	953
191	379	283	571	487	971
193	383	293	577	491	977
197	389	307	613	499	991
199	397	311	617	503	997
211	401	313	619	509	1013
		317	631	521	1039

$1822 \leqslant m \leqslant 3337$ $k=10$ or 11		$3388 \leqslant m \leqslant 4095$ $k=11$		$4096 \leqslant m \leqslant 6433$ $k=12$		$6434 \leqslant m \leqslant 12345$ $k=12$ or 13	
q_i	r_i	q_i	r_i	q_i	r_i	q_i	r_i
839	1669	1607	3203	1613	3217	3089	6173
853	1697	1609	3209	1619	3221	3109	6197
857	1699	1613	3217	1621	3229	3119	6199
859	1709	1619	3221	1627	3251	3121	6203
863	1721	1621	3229	1637	3253	3137	6211
877	1723	1627	3251	1657	3257	3163	6217
881	1733	1637	3253	1663	3259	3167	6221
883	1741	1657	3257	1667	3271	3169	6229
887	1747	1663	3259	1669	3299	3181	6247
907	1753	1667	3271	1693	3301	3187	6257
911	1759	1669	3299	1697	3307	3191	6263
				1699	3313	3209	6269
						3217	6271

LUMINESCENCE, ABSORPTION AND SCATTERING OF LIGHT IN DIAMONDS: PART II. PHOSPHORESCENCE

By P. G. N. Nayar

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received May 10, 1941

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. *Introduction*

In Part I of this paper various investigations on the fluorescence spectrum of diamond were described. The term *fluorescence* was there employed to signify the light given out by diamonds *during* excitation by light of suitable wavelength. The present paper deals with *phosphorescence* or the light emitted *after* the exciting light is cut off. Considered generally, any process of emission of light involves a small but definite interval of time which might vary within wide limits as can be seen from the fact in the case of the resonance radiation of sodium atoms the after-glow period is of the order of 10^{-8} secs. while it is as much as 10^{-4} secs. for zinc atoms. The definitions of fluorescence and phosphorescence based on the distinction of light given out *during* excitation and *after* excitation is to a certain extent arbitrary and has been the subject of much discussion recently. However, there are a great many crystals in which the times of decay are so different that it is easy to distinguish between fluorescence which disappears practically instantaneously (time of the order of 10^{-4} secs. or less) and a phosphorescence which lasts for an easily observable interval of time. It is well known that diamond is such a crystal and several investigators in the past have remarked on the property of some diamonds to glow in the dark after being exposed to light. Among these earlier workers may be mentioned Crookes who found that many of the diamonds were capable of showing phosphorescence after they had been exposed to sunlight or cathode-ray bombardment. Lines at 5030, 5130 and 5370* were observed by him in the phosphorescent light of diamond in a discharge tube. An early work due to E. Becquerel describes the spectrum as covering the region 4300–4860 and 5270–6560. The author has mentioned in the previous work that the fluorescence spectrum consists of certain well-resolved discrete bands and the present investigation was

* The figures in this page and the following pages indicate wave-lengths in A.U.

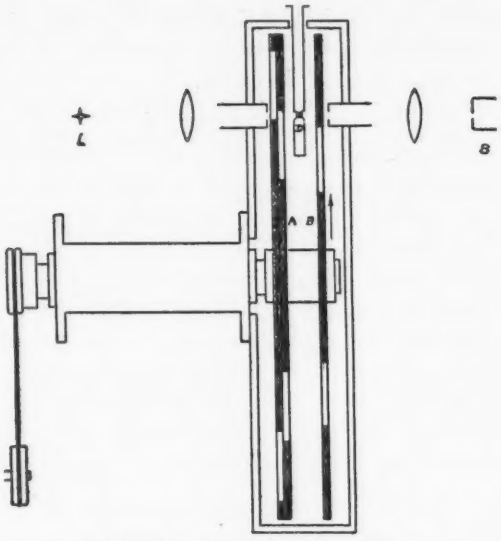
undertaken to study the relation of fluorescence to phosphorescence mainly with respect to the spectroscopic aspects, but results of observations of the time constants involved are also included.

2. *Experimental*

Specimen employed.—It was remarked by Crookes that diamonds which show the brightest phosphorescence are those that are strongly fluorescent in sunlight. This was found to be true with regard to the specimens in the collection that has been described in the previous paper. The crystal D_7 which showed brilliant fluorescence under the mercury arc also showed under proper conditions of observation a greenish yellow glow lasting for about five minutes after the excitation was cut off. D_2 which is the next in order of fluorescence also showed the phenomenon but to a much lesser extent, while in the other cases there was no noticeable effect. The crystal D_7 was therefore employed in the present investigation to record the phosphorescent spectrum using a mechanical type of phosphoroscope.

Apparatus.—The apparatus employed was on the principle of the well-known Becquerel phosphoroscope in which a set of sector wheels alternately illuminate and expose for observation the substance under study. The two essential requirements of the experimental arrangements are perfect freedom from illuminating light during observation, and the ability to vary the time interval between illumination and observation from very small values of the order of at least 10^{-3} secs. to large values of the order of a second. The first condition is specially important since the phosphorescence is so feeble compared with the fluorescence that even a small amount of diffuse light from the exciting source falling on the crystal during the time of observation would give rise to fluorescence. The details of the apparatus built for this purpose are considered worth recording and are described below (Text-Fig. 1).

Two brass discs with annular quarter segments removed were mounted on a ball-bearing axle. The first of these (A) was a composite wheel of two discs, so that by their relative disposition, the opening could be regulated. The second disc (B) was separated from the first by about one centimetre, and the diamond was mounted between the two wheels in a line with the opening from an independent support for freedom from vibration. Light from a pointolite lamp was condensed on the diamond through the opening in the first disc, and the image of the diamond was condensed on the slit of the spectrograph through the opening in the second wheel. The two discs were kept fixed relatively to each other so that the diamond was exposed to the spectrograph only when the first disc cut off the incident light. This arrangement was rotated by a motor capable of giving a speed



Text-Fig. 1.—The Phosphoroscope

L.—Light Source. *D.*—Diamond. *A B.*—Sector Wheels. *S.*—Spectrograph.

up to 2400 R.P.M. The *time-interval* between illumination and observation could be altered within fairly wide limits by adjusting the speed of the motor or the relative position of the openings or both. The *time of illumination* could be adjusted by regulating the opening in the first disc by relative rotation of its two components. The phosphoroscope was completely enclosed in a light-tight box except for small openings to let in the light and expose the diamond to the spectrograph, and all the parts were blackened suitably. With the arrangement described, stray light was completely eliminated as was evidenced by the complete absence of any mercury arc lines on the plate even after 120 hours exposure.

Pictures were obtained of the light emitted after two different intervals of time following excitation. In the first experiment, from the known speed of rotation and angular separation between the illuminating and exposing apertures, it was calculated that the diamond was illuminated for 1/160 secs. and exposed to the spectrograph 1/1600 secs. after excitation was cut off in each half-cycle. In the second experiment the speed was slowed down, and the interval was increased to 1/40 sec., the time of illumination being kept the same as before by suitable adjustment of the disc A. A Hilger constant deviation spectrograph was employed and the slit-width was kept

fairly large to reduce the exposure times, which were 40 hours and 120 hours in the two cases, using Ilford H. P. 2 plates.

3. The phosphorescence spectrum and its relation to fluorescence

The photographs obtained are illustrated in Fig. 1 plate. A picture of the fluorescence excited by ultra violet light is reproduced in (*a*) for comparison with the phosphorescent spectrum after 1/1600 secs. in (*b*) and the spectrum after 1/40 sec. in (*c*). The mercury arc spectrum with the same slit-width is inset in each case to indicate the position of the bands.

The complete change in appearance of the spectrum in passing from fluorescence to phosphorescence is obvious at first sight. As has been described previously, in fluorescence, the region between 5000 to 6300 is of negligible intensity compared with the region of the discrete bands between 4150 to about 4900. In phosphorescence, however, this faint region comes into prominence and the red end of the spectrum is of nearly the same intensity as the bands in the violet region.

Perhaps, a result of greater significance than the redistribution of intensities is the presence of common features in fluorescence and phosphorescence. In fluorescence, the presence of a system of discrete bands at 4156, 4280, 4390, 4514 and 4645 has been described before. The identical frequencies are present in the phosphorescence spectrum also. In any picture of fluorescence, the part due to phosphorescence is necessarily present and it is reasonable to assume that the faint part of the spectrum from 5050 to 6300 found in fluorescence with long exposures (Part I, Fig. 1) is really the contribution due to phosphorescence. The true fluorescence or instantaneous emission therefore would appear to consist of a discrete band at 4156 followed by four others and superposed by a continuous spectrum extending to about 4900. These frequencies persist as phosphorescence even after 1/40 of a second, and presumably more as will be shown in the next section. In addition, there is present a continuous spectrum extending to 6300 in which there is a broad band at 5200. Variations of sensitiveness of the plate in the red region makes the reality of a narrow band between 6200 and 6300 rather uncertain.

4. Time intervals of emission processes

Upper limit of fluorescence decay time.—The range of time-interval covered in the experiments described in the last section was between 1/1600 sec. and 1/40 sec. Within this fairly large range there is absolutely no change in the spectrum as is shown in the photographs (*b*) and (*c*) in Fig. 1 plate. With smaller intervals of the order of the decay time of fluorescence, we should expect the region of fluorescence to get stronger in intensity, but

the limitations of the mechanical type of phosphoroscope prevented further experiments in this direction. From the present experiments it is only possible to conclude that the fluorescence process decays in a much smaller time than 1/1600 secs.

Upper limit of phosphorescence decay time.—Photographic recording was not possible with longer intervals due to the feebleness of the glow, but some visual observations were carried out instead. The greenish-yellow phosphorescence of the diamond as revealed by the phosphoroscope remained unaltered in colour whether the interval was 1/1600 second or of the order of a second. In fact, by exposing the diamond to the mercury arc and observing it in a suitably darkened enclosure, the glow could be detected for as much as four to five minutes, the colour being the same as far as could be judged by the eye.

Effect of temperature.—Similar observations on the phosphorescence were made at higher and lower temperatures. At 150° C., even though the intensity of *fluorescence* was less, the glow after cutting off the incident light was visually brighter and lasted for a correspondingly longer interval of time of the order of 10 minutes.

On shutting off the exciting light with the crystal cooled in liquid air it was observed that the glow ceased to be visible in about 30 seconds. However on removing the crystal in the dark and allowing it to reach room temperature, the glow attained the normal intensity of phosphorescence at room temperature and decayed in the usual manner. The phosphorescence could be kept "frozen" in the crystal at low temperatures for a considerable amount of time after illumination upto a quarter of an hour or more. The glow of the crystal after irradiation at room temperature could be suppressed at any stage of its life by immersion in liquid air, and the residual part of its life was completed on regaining room temperature.

Time of illumination.—During the course of these investigations, it was noticed that after the crystal had been in the dark for some time, the maximum intensity of phosphorescence was not reached by a short period of illumination of the order of a fraction of a second. Prolonged exposure of the order of a minute was found to give a decidedly brighter initial intensity of phosphorescence and a correspondingly greater interval of visibility of the glow. The rise of intensity as well as the decay of phosphorescence in diamond is evidently a comparatively slow process.

These observations though of a qualitative character are suggestive of several lines of investigations of great interest. Whether with increasing exposure time or increasing intensity of illumination, the crystal would attain

a saturation value of fluorescence and phosphorescence are matters which require quantitative investigation. It is proposed to take up these questions as well as the exact nature of the excitation and decay curves in a further communication.

5. Excitation wave-length for phosphorescence

It was shown in the previous paper that the intense part of the fluorescence spectrum consisting of discrete bands is excited only by wave-lengths equal to or less than the wave-length of the first band at 4156. The question arises whether the same is true of the phosphorescence spectrum. Now that the faint part of the spectrum between 5050 and 6300 has been recognised as the contribution due to phosphorescence alone, the effect on this part of different exciting wave-lengths was made the subject of fresh experiments. The experimental arrangements using a monochromator and a source of white light for continuously varying the wave-length of illumination has been described already. The same procedure was followed in the present experiment also, with this difference namely that the purpose in this case was to record the region between 5050 and 6200. Because of the feebleness of this region, the monochromator and spectrograph slits were further widened to increase the intensity and the exposure time also had to be lengthened considerably.

The illuminating beam had a width of about 80 Å in the 4000 region, but due to smaller dispersion in the long wave-length region, it had a breadth of about 300 Å near 6000 for the same slit-width. The mean wave-length of the beam is referred to in describing the results in the next section. The intensity in the incandescent lamp used as source of light also progressively increases as we proceed from the violet to the red region with the result that the intensity of illumination was not constant throughout. Since the quantitative comparison of intensities was not of particular interest in this experiment, no special effort was made to overcome this difficulty.

Results.—The changes which take place in the spectrum are illustrated in a series of pictures in Fig. 2 plate where the excitation is varied from 4100 to 6000. Considering first fluorescence alone, the first two pictures show once again the same results as were obtained before, namely, a striking rise of intensity when the excitation wave-length is changed from 4100 and made to coincide with the first fluorescence band at 4156. It will be noticed however, that this rise of intensity is confined only to the fluorescence region and is not shared by the part of the spectrum between 5050 and 6300. On crossing the 4156 band to 4350, the fluorescence disappears just as was desscribed before, but a comparatively weak spectrum persists in this region

together with the part between 5050 and 6300. In fact the spectrum now looks exactly like the phosphorescence spectrum of Fig. 1 (*b* or *c*) with the system of discrete bands between 4150 and 4800 noticeably present.

These facts confirm the view already adopted that the spectrum between 5050 and 6300 and the faint discrete band system of nearly the same intensity, are of an entirely different category from the intense fluorescence which is capable of a resonance effect when illuminated by light of wave-length 4156.

The picture with exciting wave-length at 4350 (4300 to 4400) is of special interest because here there is an apparent violation of Stokes' law, because the 4156 band makes its appearance even though the excitation is of longer wave-length. This happens only when the exciting wave-length is fairly close to the 4156 band, and in the remaining pictures, the anti-stokes part disappears completely. The further pictures in the series show the absence of the short wave-length side, but that part of the spectrum which is of longer wave-length than the excitation continues to be present right up to the last picture of the series in which excitation is by 6000. The increase of intensity with 4700 excitation appears to be a genuine effect since there is no reason to suppose that there is a sudden rise of intensity of illumination in the region between 4400 and 5100 in the spectrum of the source of light.

6. *Discussion*

The foregoing experiments have made it clear that there are two distinct processes involved in the luminescence of diamond. One is an instantaneous emission of light while the other is a considerably delayed process. A separation between the two can be effected by cutting off the incident light and observing the emission of light after a time of 10^{-4} secs. or more. A second method is to use exciting radiation of a wave-length slightly longer than the head of the fluorescence bands, and recording the resulting emission of light with sufficiently long exposures. In these circumstances, the fluorescence proper which obeys the Stokes' law disappears, while the phosphorescence spectrum continues to be recorded with both stokes and anti-stokes components.

It is well known that instantaneous emission of fluorescence in solids is due to the excitation of the active centres, and broadly speaking, corresponds to the excitation of atoms to light emission in gases and vapours. Such an emission of light should have for its excitation a quantum of light of equal or higher energy than the emitted quantum. In other words, Stokes' law should be strictly obeyed. Without going into the question

of the nature of the active centres responsible for the luminescence in diamond, the results obtained so far show that the intense part of the luminescence is a true fluorescence of the same nature as the resonance radiation of atoms.

The second process is notable for the long intervals of time for its rise and decay, and the ability to remain in suspended activity at low temperatures. Taken with the fact that it is capable of being excited as anti-stokes radiation, the observations indicate that the lattice plays a predominant part, and that certain singularities in the lattice serve as points for storing up the luminescent energy. The energy levels indicated by the discrete frequencies are found in both cases and since these are found to persist even after 1/40 second or more, it is likely that the energy level differences in the band system are also associated with the lattice.

The author's best thanks are due to Professor Sir C. V. Raman for his kind and helpful interest in this work.

7. *Summary*

With a mechanical phosphoroscope, the spectrum of the light emitted by a suitable crystal of diamond after illumination is cut off has been found to consist of the same discrete bands at 4156, 4280, 4390, 4515 and 4645 found in fluorescence, together with a region of continuous spectrum extending from 5050 to 6300. The intensity of the region of discrete frequencies is found to be of the same order as that between 5050 and 6300, unlike the spectrum during excitation where the latter region is of negligible intensity. It has been found possible to conclude that the true fluorescence lasting for less than 10^{-4} secs. consists of the region of discrete bands alone.

The phosphorescence takes a time of the order of a minute, for its full excitation, and several minutes for its decay. At the temperature of liquid air, the phosphorescence disappears in a few seconds, but the luminescent energy is found to be kept stored in the crystal and is capable of being emitted when the temperature is raised again. At higher temperatures, the phosphorescence is brighter and is visible for a greater interval of time.

Using different wave-lengths of excitation, it is found that the fluorescence disappears when the wave-length is slightly longer than 4156, but a spectrum of low intensity identical with that of phosphorescence continues to be recorded. When the wave-length is only slightly longer than 4156, the anti-stokes part is also present. With further increase of wave-length, this part disappears, but that part of the spectrum which is of longer wave-length continues to be excited with undiminished intensity.

The nature of the two processes involved in the luminescence of diamond is discussed. It is pointed out that the lattice plays a predominant part in the second process and that the energy level differences in the fluorescence spectrum are also associated with the lattice.

REFERENCE

Nayar, P. G. N. .. .. *Proc. Ind. Acad. Sci.*, This issue page 483.

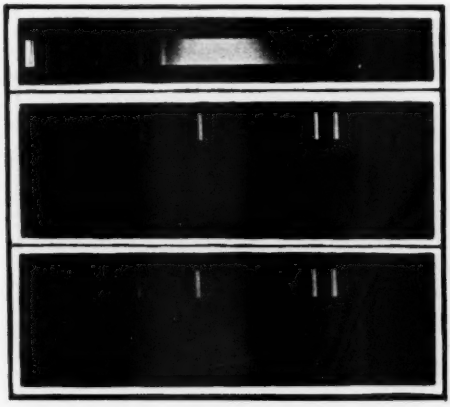


FIG. 1. Fluorescence and Phosphorescence of Diamond

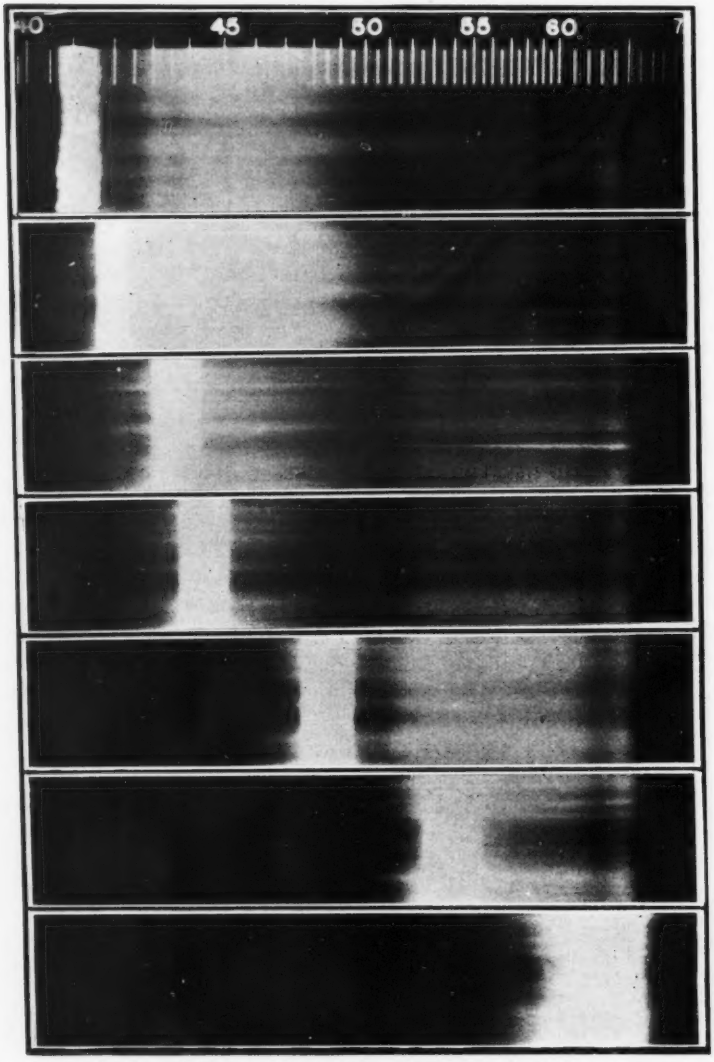


FIG. 2. Excitation of fluorescence and phosphorescence by different wave-lengths

RAMAN EFFECT IN RELATION TO CRYSTAL STRUCTURE: LATTICE OSCILLATIONS

By S. Bhagavantam

(From the Department of Physics, Andhra University, Waltair)

Received May 22, 1941

1. Introduction

It may easily be shown that when radiation falls on a block of *perfectly homogeneous* matter, there is no scattering of either the diffuse or the specular type. The validity of this statement rests on our being able to divide the entire block into a large number of volume elements which are identical with each other in all respects and each of which is quite small in comparison with the wave-length of the incident radiation. This result is, however, considerably modified in actual application as it rests on a hypothesis that can never be realized in practice. A perfect crystal, provided the temperature is sufficiently low and the incident radiation has a wave-length which is quite large in comparison with the interatomic distances, has often been given as an example closely approaching such an ideal. A little consideration will show that even this case falls short of the ideal in several respects. One of these is intimately connected with the experimental result that in crystals, Raman lines characterized by large frequency shifts are easily recorded even at very low temperatures. This implies that we cannot ignore the effect on radiation of the kinetic motions, even after eliminating them by reducing the temperature, because we have always to reckon with the possibility of the incident radiation itself inducing them.

There have been some suggestions as regards the actual condition in which the crystal should find itself, if it is to give rise to a scattered beam of an appreciable intensity. Mention may be made here of a working hypothesis, adopted by the author and Venkatarayudu (1939) in their earlier investigations, which states that only those lines which correspond to the mutual vibrations of the elementary lattices that constitute the structure have a chance of being observed in Raman scattering.

Raman and Nagendra Nath (1940) and Raman (1941) have, on the other hand, given a slightly different picture in their recent investigations. That the relation (1), originally enunciated by Brillouin (1922), is of fundamental importance in this connection as well, is an important feature of their work. λ is the wave-length of the incident light and

$$\lambda = 2\lambda^* \sin\theta \qquad (1)$$

λ^* is the wave-length of the stratification that causes a scattered beam in a direction which deviates from the incident direction by 2θ. In this picture, all diffuse scattering by crystals is in the nature of specular reflection. If λ is large, a suitable λ^* is always available for any value of θ and specular reflection, because it is thus present in all directions, may be called diffuse scattering.

In the present paper, it is proposed to briefly examine the relation between these two ways of looking at the phenomenon and extend the author's earlier work to some crystals with special reference to certain aspects that had not been dealt with in detail at that time.

2. *The Dynamic Condition of a Crystal*

If we are dealing with a crystal made up of N unit cells, there being n atoms in each of these unit cells, the well-known work of Born shows that the $3n$ N degrees of freedom may be distributed over the various normal modes of oscillation of the crystal which fall into $3n$ series. Of these $3n$ series, 3 are of the acoustic class and the rest belong to the optical class. In all these cases, stratifications which are periodic both in time and in space are caused in the medium.

In order to bring out the mutual relationships that exist between the various parameters that characterize such stratifications, we consider, for simplicity, a linear chain structure shown in Fig. 1. In this structure, each

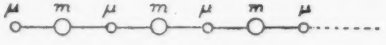


FIG. 1

one of the atoms is confined to move along the chain and has only one degree of freedom. The distance between two consecutive atoms is a and α is the restoring force called into play when this distance changes by one unit. The unit pattern in this model has a length $2a$ and contains two atoms, one of mass μ and the other of mass m. Fig. 2, taken from Born's

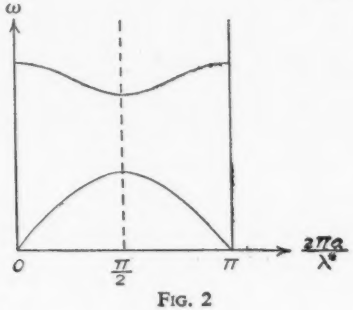


FIG. 2

work, illustrates some of the important features. The angular frequency ω or $2\pi\nu$ is plotted against the parameter $\frac{2\pi a}{\lambda^*}$. λ^* is the wave-length of the stratification. In this case, there is only one series of the optical type and one of the acoustic type. In the neighbourhood of the origin, the optical series shown by the upper curve in Fig. 2 is represented by equation (2) and the acoustic series shown by the lower curve is represented by equation (3).

$$\omega_1^2 = 2\alpha\cdot\frac{m+\mu}{m\mu} - \left(\frac{2\pi a}{\lambda^*}\right)^2\cdot\frac{2\alpha}{m+\mu} + \cdots \quad (2)$$

$$\omega_2^2 = \left(\frac{2\pi a}{\lambda^*}\right)^2\cdot\frac{2\alpha}{m+\mu} + \cdots \quad (3)$$

The lowest acoustic frequency which is equal to zero and the highest optical frequency which is equal to $\left[2\alpha\cdot\frac{m+\mu}{m\mu}\right]^{\frac{1}{2}}$ correspond to a stratification whose wave-length is the length of the chain itself and this may be regarded as infinitely large in comparison with the interatomic distances. These modes may conveniently be referred to as the limiting oscillations of the structure. The limiting optical oscillation, in particular, may be described as a motion of the whole chain of μ atoms against the whole chain of m atoms. Confining ourselves to equations (2) and (3), which are strictly valid only in the neighbourhood of the origin where λ^* is very large, it is easily seen from (3) that the velocity of the acoustic waves in the medium is about 10^6 cm. per second if the restoring force is assumed to be of the order of 10^4 dynes per cm. extension. This is of the right order of magnitude. More important than this, for our present purpose, is the fact that while the limiting optical frequency is of the order of 10^{13}, the diminution caused in it, even as we come down from $\lambda = \infty$ to $\lambda = 10^{-5}$ cm.; is only of the order of 10^{10}. This result is easily obtained from (2) and implies that the upper curve in Fig. 2 is so flat in the neighbourhood of the origin that stratifications possessing wave-lengths comparable to the wave-length of light in the visible region are characterized by frequencies which differ from the limiting frequency by only about one in a thousand.

Although the above arguments relate to the simple case of a chain, the general conclusions relating to the division of the series into the optical and the acoustic classes, the existence of the limiting oscillations corresponding to $\lambda = \infty$ characterized by special features and the flatness of the curves showing the variation of the optical frequencies with wave-length in the neighbourhood of the origin remain unaffected when the analysis is extended to three dimensional lattice structures, provided the interatomic forces continue to be of the order of 10^4 dynes per cm. extension. As a result of the

temperature which the crystal may possess, there will be thermal energy and this will be distributed amongst the various degrees of freedom in accordance with the Boltzmann law. As has already been remarked, we cannot lgnore the degrees of freedom which have a low *a priori* probability as per this law, because when radiation is incident, just those may be induced if they happen to be the appropriate ones. Thus, incident radiation possessing a large wave-length, is specularly reflected in all directions in accordance with relation (1), irrespective of the temperature of the crystal being high or low. It may, however, be noted that different stratifications possessing different values of λ^* will be effective for different values of 2θ. As 2θ ranges from being 0 in the case of forward scattering to being 180° in the case of backward scattering, the effective value of λ^* will range from ∞ in the former case to $\frac{\lambda}{2}$ in the latter. In this general case, there are $3n$ series of stratifications and one stratification possessing the required λ^* for a given λ and θ can be picked up from each of the $3n$ series. Three of these, belonging to the acoustic class, give rise to six Brillouin components whose positions are given by the well-known relation (4)

$$d\nu = \pm 2 \frac{\nu}{c} \cdot v \sin\theta \tag{4}$$

v, the velocity of sound in the medium, can take the three appropriate values which are generally different from each other. Each of the remaining $3n$-3 optical series will furnish one stratification having that particular value λ^* which will fit in with the direction of observation and the wave-length of the incident light used. In each case, provided consequent changes in the optical properties of the medium are brought about, two Raman lines given by (5) are produced

$$d\nu = \pm \nu^* \tag{5}$$

ν^* is the optical frequency corresponding to λ^* and will be quite different for different series. The important point is that while $d\nu$ in (4) depends very much on θ, $d\nu$ in (5) depends on θ only inasmuch as λ^* depends on θ. It has already been shown that even when the wave-length of the optical stratifications changes from ∞ to a dimension comparable to that of the wave-length of light in the visible region—which is indeed the range of λ^* as θ goes through all possible values—the frequency changes only by about one in a thousand. This enables us to overlook in practice, any possible dependence of the frequency of a Raman line on the direction of observation. We are further enabled to state that, while the limiting oscillation itself does not cause the diffuse scattering in any case, yet it may be chosen as a representative of a whole series, different members of which cause the

Raman line in question in practically the same position for different directions of observation.

3. *External and Internal Oscillations*

Reasons have been given to show why the limiting oscillations in a crystal may be studied as representative members of the various series. The first problem that confronts us, when we attempt to interpret the Raman spectrum of a crystal, is therefore, to find the correct unit cell.

For simplicity, let us consider in the first instance, a lattice and not a structure.† One way of choosing the unit cell, which is commonly employed in the crystallographic literature, is to choose a cell whose axes coincide with the crystallographic axes. Such a choice has the merit of clearly showing up the crystal system to which the lattice belongs. There is, however, a serious drawback in such a description because, the unit cell so chosen is not always of the smallest possible size. When the unit cell chosen is not of the smallest possible size, the labour involved in putting down the normal co-ordinates corresponding to the various limiting oscillations becomes considerable. On the other hand, if the unit cell is so chosen that its axes coincide with the primitive translations of the lattice, it is always of the smallest possible size and contains only one atom. It is immediately evident that there are no oscillations of the optical type and that no Raman scattering will be exhibited by a simple lattice.

If a crystal has a constitution which is to be regarded as a structure or a set of inter-penentrating lattices, it is easily seen that the unit cell of the smallest possible size will contain as many atoms in it as there are interpenetrating lattices in the structure. These points may be referred to as the non-equivalent points of the structure, for no one of these points may be reached from any other by performing the primitive translations characteristic of the lattice. If there are n non-equivalent points in a structure, there will be $3n-3$ optical series and in order to study the limiting oscillations of the whole crystal, we merely have to study the $3n-3$ normal oscillations of the point group constituted by the n non-equivalent points. The three excluded degrees of freedom relate to the translations of the group as a whole.

We have now to classify the $3n-3$ optical oscillations as external and internal ones. The external ones are sometimes referred to as the lattice

† The word lattice is used to denote an arrangement in which only one atom is located at each of the lattice points. A structure, on the other hand, denotes an arrangement in which a group of two or more atoms is located at each of the lattice points and has, therefore, to be looked upon as made up of a set of interpenetrating lattices.

oscillations. The distinction is not a very clear-cut one but the following may serve as useful criteria in the two cases. The possibility of the oscillations being classified in this manner rests on our being able to divide the n non-equivalent points into s groups such that the forces between one group and the other are comparatively feeble whereas the forces that exist between the members of any one group, are quite strong. In such a case, all the oscillations involving a movement of the s groups, only as entities, will generally exhibit low frequencies and may be termed external. The others, involving also movements of the individual members in each of the groups against themselves, will generally exhibit high frequencies and may be termed internal. The external oscillations may further be sub-divided into two classes, namely, rotational and translational, according as the movements of the groups are of a rotatory type or translatory type. In complicated crystals, where a full and detailed analysis is very difficult to carry through, a classification in this manner is likely to be of great help in explaining the results. In fact the purpose of the present paper is to show that the application of the group theory to a study of the limiting oscillations in a crystal enables us to classify them in the above manner and thus arrive at fruitful results even when the crystal structure is somewhat complicated. The foregoing sections constitute the necessary background and we shall now derive some important theorems and apply them to specific cases of practical interest.

4. *Application of Group Theory*

In all that follows, we need consider only the group of n non-equivalent points that are contained in the unit cell formed by taking for its sides, the primitive translations of a lattice or a structure as the case may be. The covering operations constitute a group and the Character Table with the irreducible representations of the group may easily be written out. Relation (6) enables us to find n_i, the number of times a particular irreducible representation Γ_i is contained in another representation Γ, if the group characters in both the representations are known.

$$n_i = \frac{1}{N} \sum_j h_j \chi_i(R) \chi_j'(R) \qquad (6)$$

$\chi_i(R)$ and $\chi_j'(R)$ are respectively the characters of the group operation R in the representations Γ_i and Γ and N is the order of the group and h_j is the number of group operations falling under the jth class. One of the main results of the present investigation follows from the fact that by suitably choosing the representation Γ and utilizing the characters $\chi_j(R)$ appropriate to it, we can confine ourselves to one or other of the several types of normal oscillations.

For example, if Γ is a representation defined by all the $3n$ cartesian co-ordinates which account for the entire freedom possessed by the n non-equivalent points in the unit cell, then

$$\chi_i'(\mathrm{R}) = \omega_{\mathrm{R}} (\pm 1 + 2\cos\phi_{\mathrm{R}}) \tag{7}$$

and n_i, obtained by substituting (7) in (6), will include all types of normal modes, namely, translations, translatory and rotatory types of external oscillations and internal oscillations. (7) is a relation which is now well known and the method of deriving it has been given in the earlier literature already referred to. It will be evident from the linear transformation given below:

$$x \rightarrow x\cos\phi + y\sin\phi; \quad y \rightarrow -x\sin\phi + y\cos\phi; \quad z \rightarrow \pm z.$$

ω_{R} is the number of atoms that remain invariant under the operation R and the plus or the minus sign is to be used according as R is a pure rotation through ϕ or a rotation through ϕ accompanied by a reflection. The atoms that change position under the operation R do not contribute to the character.

If we want to confine ourselves only to translations (acoustic series), it is clear that ω_{R} is to be put equal to unity for all R because the whole group moves as one entity in these modes. In other words, Γ is defined by only three cartesian co-ordinates and it is easily seen that

$$\chi_i'(\mathrm{R}) = \pm 1 + 2\cos\phi_{\mathrm{R}} \tag{8}$$

n_i obtained by substituting (8) in (6) may be denoted as $n_i(\mathrm{T})$, as the results now refer to translations or the acoustic series only.

Relation (9) gives the value of $\chi_i'(\mathrm{R})$, if we confine ourselves to the translatory type of external oscillations. As has already been explained in section 3, s is the number of groups into which the non-equivalent points may be divided, with due regard to the magnitudes of the forces that exist between them.

$$\chi_i'(\mathrm{R}) = [\omega_{\mathrm{R}}(s) - 1](\pm 1 + 2\cos\phi_{\mathrm{R}}) \tag{9}$$

$\omega_{\mathrm{R}}(s)$ represents the number of such groups that remain invariant out of the number s under an operation R. The derivation of (9) is quite simple. Each one of the groups s has 3 degrees of translational freedom and the representation Γ in this case is defined by $3s$ cartesian co-ordinates. $\omega_{\mathrm{R}}(s)(\pm 1 + 2\cos\phi_{\mathrm{R}})$ will be the character of an operation R in such a representation. If the pure translations that have already been taken account of in (8) are to be excluded from this, we have to subtract $\pm 1 + 2\cos\phi_{\mathrm{R}}$ from $\omega_{\mathrm{R}}(s)(\pm 1 + 2\cos\phi_{\mathrm{R}})$ and we get (9).

Relation (10) gives the value of $\chi_i'(\mathrm{R})$, if we confine ourselves to the rotatory type of external oscillations. p in (10)

stands for the number of groups in s, which are constituted by

$$\chi_i'(\mathrm{R}) = [\omega_\mathrm{R}(s-p)](1 \pm 2\cos\phi_\mathrm{R}) \qquad (10)$$

single atoms only. Such monatomic groups have no rotational degrees of freedom and $s-p$ is, therefore, the number of groups with each of which we have to associate three degrees of rotational freedom. $\omega_\mathrm{R}(s-p)$ represents the number that remain invariant out of the number $s-p$ under an operation R. The derivation of (10) is also quite simple. It has already been shown by Rosenthal and Murphy (1936) that the character of an operation R, in a representation defined by the three components of an angular momentum vector, is $1 \pm 2\cos\phi_\mathrm{R}$ according as R is a pure rotation through ϕ or a rotation through ϕ accompanied by a reflection. This is evident from the transformations given below:

$$l_x \rightarrow \pm l_x\cos\phi \pm l_y\sin\phi; \quad l_y \rightarrow \mp l_x\sin\phi \pm l_y\cos\phi; \quad l_z \rightarrow l_z$$

l_x, l_y and l_z are the components of the angular momentum and the series of signs given on the top are to be taken when the operation R is a pure rotation around the Z axis. The alternative set relates to the case where R is a rotation accompanied by a reflection. If there are $\omega_\mathrm{R}(s-p)$ separate units, each of which has three degrees of rotational freedom, the representation will be that defined by $3\,\omega_\mathrm{R}(s-p)$ components of angular momentum and the character of an operation R in such a representation is that given by (10). Those groups which are not invariant under the operation R do not contribute to the character.

In order to get n_i', the number of internal oscillations under each representation, we merely have to eliminate those given under the categories (8), (9) and (10) from n_i obtained by using (7). This is formally achieved by writing out the character as given by (11) and using it in the formula (6). The result may also be obtained by direct subtraction of the numbers under the categories of translation and translatory and rotatory types of external oscillations from the total number under each representation.

$$\chi_i'(\mathrm{R}) = [\omega_\mathrm{R} - \omega_\mathrm{R}(s)](\pm 1 + 2\cos\phi_\mathrm{R}) - \omega_\mathrm{R}(s-p)(1 \pm 2\cos\phi_\mathrm{R}) \qquad (11)$$

5. *Calcite and Sodium Nitrate*

In order that the utility of the above method may be fully appreciated, we shall first apply it to the well-known cases of calcite and sodium nitrate in this section. These two substances have the same crystal structures and their space group is D^6_{3d}. Exactly similar considerations apply to both. The unit cell which is shown in Fig. 3 is an elongated rhombohedron and contains two molecules. The lattices are ionic and the co-ordinates of the atoms in the case of calcite are given below.

Ca (1, 2): $\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}$; $\frac{3}{4}\ \frac{3}{4}\ \frac{3}{4}$
C (3, 4): 0 0 0; $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$
0 (5 to 10)

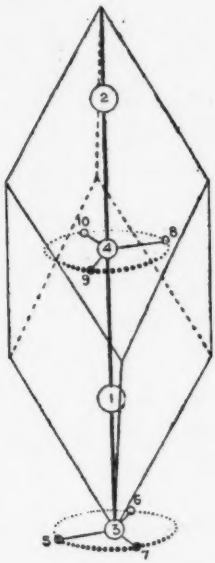


FIG. 3

In the notation of the present paper, $n = 10$, $s = 4$ (two CO_3 groups and two Ca atoms) and $p = 2$ (two Ca atoms).

The operations of this group may be expressed as follows:

E (Identity)

$2\,S^{1}_{4}$ {(1) (2) (3, 4) (5, 9, 7, 8, 6, 10)
(1) (2) (3, 4) (5, 10, 6, 8, 7, 9)

$2\,C^{1}$ {(1) (2) (3) (4) (8, 10, 9) (5, 7, 6)
(1) (2) (3) (4) (8, 9, 10) (5, 6, 7)

i (1) (2) (3, 4) (5, 8) (6, 9) (7, 10)

$3\sigma_v$ (glide) {(1, 2) (3, 4) (5, 8) (6, 10) (7, 9)
(1, 2) (3, 4) (5, 10) (6, 9) (7, 8)
(1, 2) (3, 4) (5, 9) (6, 8) (7, 10)

$3\,C_2$ {(1, 2) (3) (4) (5) (8) (6, 7) (9, 10)
(1, 2) (3) (4) (6) (9) (5, 7) (8, 10)
(1, 2) (3) (4) (7) (10) (5, 6) (8, 9)

The Character Table and the values of n_i, n_i', etc., are given below:

D^6_{2d}	E	$2S_4^1$	$2C^1$	i	$3\sigma_v$	$3C_2$	External n_i	T	T′	R′	n_i'	Raman	Infra-red
A_1 ..	1	1	1	1	1	1	1	0	0	0	1	p	f
A_2 ..	1	1	1	1	−1	−1	3	0	1	1	1	f	f
B_1 ..	1	−1	1	−1	1	−1	4	1	1	1	1	f	p
B_2 ..	1	−1	1	−1	−1	1	2	0	1	0	1	f	f
E_1 ..	2	1	−1	−2	0	0	6	1	2	1	2	f	p
E_2 ..	2	−1	−1	2	0	0	4	0	1	1	2	p	f
$\omega_R(n_i)$ ..	10	2	4	2	0	4							
$\omega_R(s)$ ..	4	2	4	2	0	2							
$\omega_R(s-p)$	2	0	2	0	0	2							
$h_j\chi_j'(n_i)$ ..	30	0	0	−6	0	−12							
$h_j\chi_j'(T)$ ..	3	0	0	−3	3	−3							
$h_j\chi_j'(T')$ ..	9	0	0	−3	−3	−3							
$h_j\chi_j'(R')$ ..	6	0	0	0	0	−6							

In this and other tables that follow, n_i, T, T′, R′ and n_i' stand for the total number of oscillations, translations, translatory type of external oscillations, rotatory type of external oscillations and the internal oscillations respectively. $\chi_j'(n_i)$, $\chi_j'(T)$, $\chi_j'(T')$ and $\chi_j'(R')$ have been obtained in accordance with the values given for them in the relations (7), (8), (9) and (10) respectively. The method of finding out whether the lines coming under a certain representation are Raman active or infra-red active has been described in the earlier literature and we need not go into it here. p denotes that all the oscillations coming under that representation are permitted to appear and f denotes that they are forbidden. The following features may now be noted. Because there are two CO_3 ions in the unit cell, each internal oscillation of the free CO_3 ion splits into two in the crystal. The extent of splitting will naturally depend upon the forces that are present in the crystal. Since $s=4$, besides the translations which represent the acoustic series, there are present a large number of external oscillations, both of the rotatory type and the translatory type. If we are not immediately interested in the internal oscillations, it is quite easy to picture the external modes coming under each representation in them, because all the four groups are to be regarded as entities. Only the CO_3 ions take part in the rotatory type of external

oscillations as the calcium ions (monatomic groups) come under the *p* class. As an example, we give below the symbolic representation of the two external modes coming under the representation E_2 and which are Raman active.

$$\left.\begin{aligned} T'(a) &= x_3 - x_4 \\ T'(b) &= y_3 - y_4 \\ R'(a) &= l^3{}_x + l^4{}_x \\ R'(b) &= l^3{}_y + l^4{}_y \end{aligned}\right\} \cdots\cdots E_2$$

$T'(a)$ and $T'(b)$ and similarly $R'(a)$ and $R'(b)$ are degenerate. Z axis is taken along the trigonal axis and the X and Y axes may lie anywhere in the plane perpendicular thereto. x_3 indicates that the group containing atom 3 undergoes a displacement of one unit in the direction of the X axis. x_4, y_3, etc., occurring in the normal co-ordinates relating to the T′ type are to be similarly interpreted. $l^3{}_x$ indicates that the group containing atom 3 undergoes a rotation such that it possesses unit angular momentum around the X axis. $l^4{}_x$, $l^3{}_y$, etc., occurring in the normal co-ordinates relating to the R′ type are to be similarly interpreted. The method of writing down these normal co-ordinates is quite easy and is explained elsewhere. With the help of the group operations and the transformation matrices for x, y z and l_x, l_y, l_z already given in a foregoing section, it may be verified that the characters of the normal co-ordinates given above for various R are just those given under the irreducible representation E_2. One of these modes is represented diagrammatically in Fig. 4. They are identical with the modes

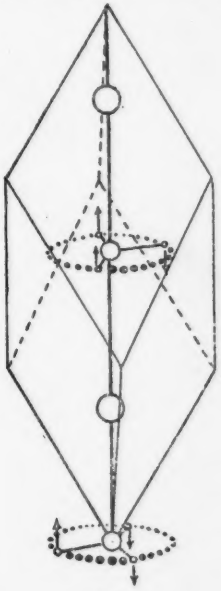


FIG. 4

obtained by a more elaborate method and described in an earlier paper by the author and Venkatarayudu (1939) as Q_{15} and Q_{17}.

In a similar manner, we can write down the normal co-ordinates relating to all the external oscillations without much labour and without reference to the internal modes. Such an investigation need not be pursued for this case as the results are already well known. In fact, if only the external modes and their classification are needed, the group operations also could have been written in a much simpler manner as will be evident from the cases that are dealt with in the following sections.

6. *Some Special Cases*

Such a simplification will be particularly useful, when experimental results show that the intermolecular forces in the crystal are not very important. This may easily be inferred, especially in cases where there is no degradation of symmetry from the free molecule to the crystal, if we find that the Raman lines obtained in the liquid exhibit a general one to one correspondence with those obtained in the same substance in the crystalline state even though there may be two or more molecules per unit cell in the latter.* In such cases, no more information will be obtained by making a detailed study of the internal frequencies for a group of molecules than that available from a study of the single molecule. On the other hand, much of the interest will centre round the lattice oscillations and the special methods outlined in the foregoing pages will be particularly useful. The classification of the lattice oscillations into the translatory and the rotatory types is also of some help, if the following principles are borne in mind in interpreting the experimental results. The translatory type of oscillations are likely to give rise to relatively low frequencies in most cases and even these will be of low intensity in Raman scattering as the changes caused in the polarizability of the crystal cannot be appreciable. On the other hand, the rotatory type of oscillations will result in intense Raman lines, if the rotating groups are strongly optically anisotropic.

1. *If there is only one molecule per unit cell and if centre of inversion is a covering operation of the structure, the crystal may exhibit three lattices oscillations of the rotatory type if there is no degeneracy.*

This statement is almost self-evident and follows from the fact that the three oscillations of the rotatory type are symmetric to the operation of

* The resemblance referred to is of a general nature. One or two of the lines that occur in the crystal may not appear in the liquid and *vice versa* on account of the different symmetries in the two cases. The essential point is that there is no splitting of the majority of the lines as we pass from the liquid to the crystal.

inversion. For crystals of trigonal, tetragonal and hexagonal classes, this number reduces to two and for crystals of the cubic class, it reduces to one merely as a result of the symmetry. As the intensity will also be governed by the optical anisotropy of the molecule, the only lattice line in the case of cubic crystals will have zero intensity because the molecule itself should possess cubic symmetry and one of the lattice lines (non-degenerate one) in the trigonal, tetragonal and hexagonal classes will also have zero intensity.

2. *If there are two molecules per unit cell and if the centre of inversion, as a covering operation of the structure, is located at one of the molecules, all lattice oscillations of the translatory type will be Raman inactive. Some of them may be infra-red active.*

This follows from the fact that the normal co-ordinates relating to such oscillations, are always anti-symmetric to the operation of inversion.

3. *If in the above case, the centre of inversion is located midway between the two molecules, all lattice oscillations of the translatory type will be symmetric to the operation of inversion and some of them may be Raman active. All of them will be infra-red inactive.*

7. *Naphthalene, Diphenyl, Anthracene, etc.*

All the substances discussed in this section crystallize in the monoclinic prismatic class having the space group C_{2h}^5. The unit cell in each case contains two molecules. They have been specially chosen here with a view to bring out the fact that the crystal structure plays a major part in determining the character of the low frequency Raman spectrum while the exact chemical nature of the substance has no appreciable influence on it. We start by stating that these crystals melt at comparatively low temperatures and that the Raman lines of naphthalene in the liquid state show a one to one correspondence with those obtained in the crystal (Nedungadi, 1941). Lines do not show any systematic doubling even though there are two molecules in the unit cell. A study of the internal oscillations may, therefore, be confined with advantage to the free molecule. We shall now apply the methods of the foregoing sections to these cases and obtain the results that are to be expected in the low frequency region of the Raman spectrum. Fig. 5 represents the unit cell for naphthalene which is a typical representative of this class. The two molecules are numbered 1 and 2. In the notation of the present paper, $s = 2$ and $p = 0$. These molecules have their lengths roughly parallel to the C axis and their planes making angles of about $+ 65°$

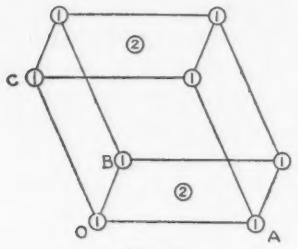


FIG. 5

and $-65°$ with the (010) plane. The group operations may be written out as

E (Identity)
C_2 (screw) · · · · (1, 2)
i · · · · · · · · (1) (2)
σ_h (glide) · · · · (1, 2)

The Character Table and other relevant features are given below :—

$C_{2h}{}^5$	E	C_2	i	σ_h	External T	T′	R′	Raman	Infra-red
A_1 ..	1	1	1	1	0	0	3	p	f
A_2 ..	1	−1	1	−1	0	0	3	p	f
B_1 ..	1	1	−1	−1	1	2	0	f	p
B_2 ..	1	−1	−1	1	2	1	0	f	p
ω_R (s) ..	2	0	2	0					
ω_R ($s-p$)	2	0	2	0					
$h_j\chi_j'$ (T) ..	3	−1	−3	1					
$h_j\chi_j'$ (T′) ..	3	1	−3	−1					
$h_j\chi_j'$ (R′)	6	0	6	0					

Centre of inversion in this case is located at the molecule 1 and it comes under special case number 2 of the previous section. We do not get any Raman active lattice oscillations of the translatory type. We should, however, expect six oscillations of the rotatory type. The corresponding normal co-ordinates may easily be written out in the following manner:—

$$\left.\begin{matrix} l_x^1 - l_x^2 \\ l_y^1 - l_y^2 \\ l_z^1 + l_z^2 \end{matrix}\right\} \cdots A_1 ; \quad \left.\begin{matrix} l_x^1 + l_x^2 \\ l_y^1 + l_y^2 \\ l_z^1 - l_z^2 \end{matrix}\right\} \cdots A_2$$

The symmetry axis is chosen as the Z axis and any two mutually perpendicular directions in the *ac* plane may be chosen as the X and Y axes. It may be seen that the three modes coming under A_1 differ from those coming under A_2 only in the matter of the relative phase difference between the two molecules. For example, while in A_1 both molecules are rotating about the Z axis in phase, in A_2, they do so in opposite phases. As has already been said, if the intermolecular forces are not appreciable, the frequencies of these two types of motions cannot differ very much from each other and we can only expect to record three broad bands. Results are not available for anthracene. The lattice oscillations observed in naphthalene, diphenyl, *p*-dichlorobenzene and *p*-dibromobenzene, all of which belong to this class, are given below:

Naphthalene	45	73	109 and 124
Diphenyl	49	75	150
p-Dichlorobenzene	43	55	82
p-Dibromobenzene ..	38	..	93

The figures given are in cm.$^{-1}$ and in most cases, the lines are broad. The general similarity is clear. A line at about 20 cm.$^{-1}$, recorded by Vuks (1937) in the last two substances, is not included in the above table as it has not been confirmed by other investigators. The highest frequency in naphthalene has split into two, apparently because of its nearness to the sum of the other two frequencies at 45 and 73. Since all the three lines are expected to be complex in structure and as they all come under the same representation, it will be incorrect to assign any one of the frequencies to a particular mode. It is accordingly not easy to predict their behaviour under directional excitation. Consequently, one may not expect in these cases, such a clear-cut classification of the lattice oscillations into the symmetric, the anti-symmetric and the degenerate types as has been obtained in simpler structures like calcite and sodium nitrate. The high intensity of the Raman line at 73 in naphthalene suggests that it arises from rotatory movements of the molecules about the *b* axis ($l_z^1 \pm l_z^2$) because the largest optical anisotropy of the naphthalene crystal is in the *ac* plane.

8. *Effect of Crystal Modification on the Low Frequency Spectrum*

Several attempts have been made to detect changes in the Raman spectrum of a substance as we pass from one crystalline modification to another. On account of experimental difficulties these have been mostly

confined hitherto, to the internal oscillations although prominent changes are not to be expected in that region but should be looked for only in the low frequency region. In order to illustrate this point, we shall consider here the cases of aragonite and potassium nitrate. The crystal structure of aragonite bears to that of calcite, the same relationship as that existing between the structures of potassium nitrate and sodium nitrate. Unfortunately, the lattice oscillations of these substances have not been studied in detail in their Raman spectra and only meagre and conflicting results are available. Hence it is not proposed to compare the conclusions with the experimental data. Nevertheless, the analysis is given here as the structures are of great importance.

The space group is V_h^{16} and the unit cell of the smallest size, a projection of which is shown in Fig. 6, contains 4 molecules of $CaCO_3$. Since we are interested only in the lattice oscillations, we need consider 8 groups ($s = 8$) on the whole, of which 4 ($p = 4$) are monatomic.*

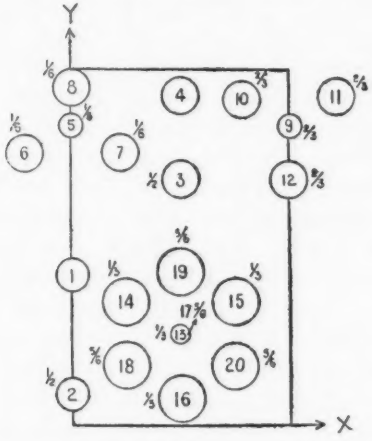


FIG. 6

The groups are numbered as follows:

Ca .. 1, 2, 3 and 4
CO_3 .. 5, 9, 13 and 17

Atoms numbered, 6, 7, 8, 10, 11, 12, 14, 15, 16, 18, 19, 20 are the oxygens and they need not be considered separately as they go with the corresponding carbons.

* The internal oscillations in this case have been considered in an earlier paper.

The operations of the group are:

E	(Identity)	
C_2	(screw $\parallel^l$ to Z)	(1, 2) (3, 4) (5, 9) (13, 17)
C_2	(screw $\parallel^l$ to Y)	(1, 4) (2, 3) (5, 17) (9, 13)
C_2'	(screw $\parallel^l$ to X)	(1, 3) (2, 4) (5, 13) (9, 17)
i	.. .. ..	(1, 2) (3, 4) (5, 9) (13, 17)
σ_h	.. .. ..	(1) (2) (3) (4) (5) (9) (13) (17)
σ_v	(glide)	(1, 3) (2, 4) (5, 13) (9, 17)
σ_v'	(glide)	(1, 4) (2, 3) (5, 17) (9, 13)

The Character Table and other relevant features are given below:

V_h^{13}	E	C^1	C_2	C_2'	i	σ_h	σ_v	σ_v'	External T	T′	R′	Raman	Infra-red
A_{1g} ..	1	1	1	1	1	1	1	1	0	4	1	*p*	*f*
A_{2g} ..	1	−1	1	−1	1	−1	1	−1	0	2	2	*p*	*f*
B_{1g} ..	1	1	−1	−1	1	1	−1	−1	0	4	1	*p*	*f*
B_{2g} ..	1	−1	−1	1	1	−1	−1	1	0	2	2	*p*	*f*
A_{1u} ..	1	1	1	1	−1	−1	−1	−1	0	2	2	*f*	*f*
A_{2u} ..	1	−1	1	−1	−1	1	−1	1	1	3	1	*f*	*p*
B_{1u} ..	1	1	−1	−1	−1	−1	1	1	1	1	2	*f*	*p*
B_{2u} ..	1	−1	−1	1	−1	1	1	−1	1	3	1	*f*	*p*
ω_R (*s*) ..	8	0	0	0	0	8	0	0					
ω_R (*s*−*p*)	4	0	0	0	0	4	0	0					
$h_j\chi_j'$ (T)	3	−1	−1	−1	−3	1	1	1					
$h_j\chi_j'$ (T′)	21	1	1	1	3	8	−1	−1					
$h_j\chi_j'$ (R′)	12	0	0	0	0	−4	0	0					

We see from the table that, besides a large number of translatory type of oscillations, we should expect to get in the Raman spectrum, six oscillations of the rotatory type under different classes. These six normal co-ordinates are easily written down in the following manner:

$$
\begin{aligned}
& l^5_z + l^9_z - l^{13}_z - l^{17}_z && \cdots\cdots A_{1g} \\
& \left.\begin{matrix} l^5_x + l^9_x - l^{13}_x - l^{17}_x \\ l^5_y + l^9_y + l^{13}_y + l^{17}_y \end{matrix}\right\} && \cdots\cdots A_{2g} \\
& l^5_z + l^9_z + l^{13}_z + l^{17}_z && \cdots\cdots B_{1g} \\
& \left.\begin{matrix} l^5_x + l^9_x + l^{13}_x + l^{17}_x \\ l^5_y + l^9_y - l^{13}_y - l^{17}_y \end{matrix}\right\} && \cdots\cdots B_{2g}
\end{aligned}
$$

Normal co-ordinates coming under A_{1g} and B_{1g}, although Raman-active, involve rotations of the CO_3 groups about the Z axis and since the XY plane is nearly a plane of optical symmetry, we can confidently conclude that these modes will not produce appreciable intensities in Raman scattering. Under A_{2g} and B_{2g}, we should expect four lines appearing as two close doublets or two broad bands covering the whole series. Their behaviour, under directional excitation, will be markedly reciprocal to that of the total symmetric internal oscillations. Besides these, we may expect a few lines arising from the translatory type of oscillations. They will be characterized by comparatively low frequencies and possibly in some cases a behaviour which is not reciprocal to that of the total symmetric oscillation.

9. *Crystals Containing Linear Molecules*

As a typical example of this class, we shall choose mercurous chloride. This substance crystallizes in the tetragonal system under the space group D^{17}_{4h}. The tetragonal unit cell contains two molecules of Hg_2Cl_2 and the lattice is molecular but the unit cell of the smallest possible size contains only one molecule. The formulæ given in the foregoing sections do not apply to this case as the molecule is linear and is a special type of group having only two degrees of rotational freedom. It is, however, clear that there will be no lattice oscillations of the translatory type and there will be only one doubly degenerate external oscillation of the rotatory type. The crystal structure of this substance is shown in Fig. 7. The group operations,

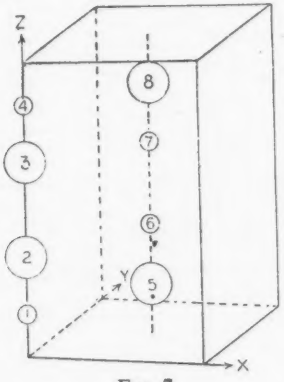


FIG. 7

Character Table, etc., are given below in full* so as to cover the internal oscillations also.

Mercury atoms are numbered 1 and 4. Chlorine atoms are numbered 2 and 3. 6 and 7 are equivalent to 1 and 4. 5 and 8 are equivalent to 2 and 3. In this case $s=1$ and $p=0$. The operations of the group are:

E	..	(Identity)
$2C^1$	..	(1) (2) (3) (4)
C^2	..	(1) (2) (3) (4)
$2C_2$	..	(14) (23)
$2C_2'$	..	(14) (23)
i	..	(14) (23)
$2S^1$	..	(14) (23)
σ_h	..	(14) (23)
$2\sigma_v$	..	(1) (2) (3) (4)
$2\sigma_v'$	..	(1) (2) (3) (4)

D_{4h}^{17}	E	$2C^1$	C^2	$2C_2$	$2C_2'$	i	$2S^1$	σ_h	$2\sigma_v$	$2\sigma_v'$	External n_t	T	T′	R′	n_i'	Raman	Infrared
A_{1g} ..	1	1	1	1	1	1	1	1	1	1	2	0	0	0	2	*p*	*f*
A_{2g} ..	1	1	1	−1	−1	1	1	1	−1	−1	0	0	0	0	0	..	..
B_{1g} ..	1	−1	1	1	−1	1	−1	1	1	−1	0	0	0	0	0	..	..
B_{2g} ..	1	−1	1	−1	1	1	−1	1	−1	1	0	0	0	0	0	..	..
E_{1g} ..	2	0	−2	0	0	2	0	−2	0	0	2	0	0	1	1	*p*	*f*
A_{1u} ..	1	1	1	1	1	−1	−1	−1	−1	−1	0	0	0	0	0	..	..
A_{2u} ..	1	1	1	−1	−1	−1	−1	−1	1	1	2	1	0	0	1	*f*	*p*
B_{1u} ..	1	−1	1	1	−1	−1	1	−1	−1	1	0	0	0	0	0	..	..
B_{2u} ..	1	−1	1	−1	1	−1	1	−1	1	−1	0	0	0	0	0	..	..
E_{1u} ..	2	0	−2	0	0	−2	0	2	0	0	2	1	0	0	1	*f*	*p*
ω_R ..	4	4	4	0	0	0	0	0	4	4							
ω_R (*s*) ..	1	1	1	1	1	1	1	1	1	1							
$h_i\chi_i'$ (n_i)	12	8	−4	0	0	0	0	0	8	8							
$h_i\chi_i'$ (T)	3	2	−1	−2	−2	−3	−2	1	2	2							
$h_i\chi_i'$ (T′)	0	0	0	0	0	0	0	0	0	0							

* Although, in this paper, we are mainly dealing with the lattice oscillations, this case is considered in some detail with a view to correct some of the mis-statements made in the earlier paper (Reference 1). These have arisen on account of the fact that a larger unit cell than is proper had been wrongly chosen at that time.

Corresponding to the 12 degrees of freedom of the four atoms in the unit cell, we get three translations (acoustic series), three single and three doubly degenerate limits (optical series) of which one is an external oscillation of the rotatory type and is Raman active. The normal co-ordinates are given below:

$$\left.\begin{aligned} Q_1'(i) &= m_2(z_1 - z_4) + m_1(z_2 - z_3) \\ Q_2'(i) &= z_1 - z_4 - z_2 + z_3 \end{aligned}\right] \quad \cdots\cdots A_{1g}$$

$$\left.\begin{aligned} Q_x(T) &= x_1 + x_2 + x_3 + x_4 \\ Q_y(T) &= y_1 + y_2 + y_3 + y_4 \\ Q_{4a}'(i) &= m_2(x_1 + x_4) - m_1(x_2 + x_3) \\ Q_{4b}'(i) &= m_2(y_1 + y_4) - m_1(y_2 + y_3) \end{aligned}\right] \quad \cdots\cdots E_{1u}$$

By altering the signs of terms with suffixes 2 and 4 in the normal co-ordinates occurring under A_{1g}, we obtain Q_z and Q_3' (i) coming under A_{2u}. Similarly, we obtain Q_{5a}' (i), Q_{6a}' (L) and their b-components coming under E_{1g} from those given under E_{1u}.

Q_{6a}' (L) and its b-component represent the rotatory type of external oscillation. This is likely to give rise to an intense Raman line but probably of a very low frequency. It has not so far been recorded. Besides this, we should expect three Raman lines of the internal type, two of which are of the total symmetric class and the third is of the degenerate class. Three strong lines at 165 (6), 273 (4) and 295 (1) have been observed in the Raman spectrum of Hg_2Cl_2 crystals. The two higher frequencies may be identified with those coming under A_{1g} whereas the one at 165 may be identified with the degenerate oscillation. An additional weak line at 320 has also been recorded and this is probably the overtone of the forbidden fundamental ν_4 whose value, by analogy with the case of acetylene and such other molecules, may be expected to lie close to 165.

10. Summary

In spite of what has occasionally been stated in the literature (Sirkar, 1937), it is believed that there are no special reasons to assume that the low frequency lines that occur in the Raman spectra of crystals have an origin that is essentially different from that ascribed to the high frequency lines. They are all regarded as representatives of the various optical series into which the normal oscillations of a crystal may be divided. Reasons have been given to show why the limiting oscillation in each series may be selected as a representative of that whole series and its characters studied. For convenience in description, these are divided into three classes, namely, the internal, the rotatory type of external and the translatory type of external

ones. Formulæ, which help us to classify the normal oscillations in the above manner, are developed and applied to some typical cases.

In interpreting the results, two guiding principles are to be borne in mind. All the oscillations coming under the translatory type, especially, in organic crystals and others of low melting point, will be characterized by low or vanishingly small frequencies and the corresponding Raman lines, if they occur at all, will be weak. On the other hand, those coming under the rotatory type will be characterized by relatively large frequencies and generally give rise to strong Raman lines if the rotating group has a marked optical anisotropy. Since the region under investigation is, however, very crowded, we should expect several complications such as overlapping, splitting, etc., to set in, and these make the interpretation of the experimental results somewhat difficult.

The author desires to express his thanks to Prof. Sir C. V. Raman and Dr. N. S. Nagendra Nath with whom he had the opportunity of discussing some of the ideas contained in this paper.

REFERENCES

Bhagavantam and Venkatarayudu		*Proc. Ind. Acad. Sci.*, 1939, **9**, 224.
Brillouin	..	*Annales De Physique*, 1922, **17**, 88.
Nedungadi	..	*Proc. Ind. Acad. Sci.*, 1941, **13**, 161.
Raman	..	*Ibid.*, 1941, **13**, 1.
—— and Nagendra Nath	..	*Ibid.*, 1940, **12**, 83.
Rosenthal and Murphy	..	*Rev. Mod. Phys.*, 1936, **8**, 317.
Sirkar	..	*Ind. Jour. Phys.*, 1937, **10**, 109.
Vuks	..	*Acta Physico-chemica*, 1937. **6**, 11.

PAPER PULP FROM ANNUAL CROPS

Part II. A Note on the Yields and Characteristics of Pulps from Different Varieties of Rice Straw.

By P. Bhaskara Rama Murti

(From the Department of Chemical Technology, Andhra University, Waltair)

Received April 22, 1941

(Communicated by Prof. T. R. Seshadri)

In continuation of work described in Part I[1] large quantities of straw available locally in the market were treated for the production of paper pulp. It was noticed that the yield and the quality of the pulp obtained was poor and hence there was indication that the quality of straw varies considerably in regard to the production of paper pulp. This may explain the observations of certain workers that rice straw is not quite suitable for paper manufacture.[2] They might have been dealing with straw of very poor quality. Table I gives a comparison of the local sample (A) now examined by boiling with 3% alkali solution for 3 hours at 130°, with the composite sample obtained from Samalkota (B) and already described in Part I.

Table I

Treatment NaOH % on straw	Yield of unbleached pulp on straw %		Yield of bleached pulp on straw %		α-cellulose in pulp %		Consumption of available Cl_2 on pulp %	
	A	B	A	B	A	B	A	B
30	32·0	41·5	29·6	38·2	80·0	80·0	4·7	4·5
22	33·0	43·5	30·8	41·5	76·0	77·7	4·9	4·7
15	35·0	46·5	31·4	44·0	76·8	77·1	6·0	5·9
Double boiled	33·5	44·0	31·8	42·0	72·2	77·6	4·0	3·6

From the above table it is clear that the yields of pulp under various treatments are uniformly and considerably lower in sample (A) as compared with sample (B). Though the characteristics of the pulps from the two samples are similar as far as the cellulose content and bleach consumption are concerned, the pulp from (A) could not be bleached to

standard whiteness. Consequently work has now been undertaken to examine straw from the most important varieties of rice grown in the Godavari and Kistna deltas. They were obtained from the Agricultural research station, Samalkota, and they were the components of the composite sample (B). Table II embodies the results relating to the chemical composition of different varieties of rice straw. They were the average of duplicates which were found to be closely agreeing.

TABLE II

Name of the variety	Moisture %	Lignin %	Pentosans %	C & B cellulose %
Punasakonamani ..	12·2	25·0	21·7	39·3
Punasa Akkullu ..	11·8	31·2	22·9	37·4
Konamani ..	12·1	28·2	19·8	41·2
G. E. B. 24 straw ..	12·0	31·8	23·7	36·4
Composite sample (B) ..	12·0–12·2	25·0–28	20–22·0	37·5–38·2
Local sample (A) ..	12·5	25·2	26·1	28·8–30·0

Though small differences exist in varieties grown under the same conditions of soil and cultivation more marked changes seem to be brought about by variations in the soil and cultivation.

It has been already pointed out in regard to work on the composite sample (B) that the characteristics of the pulp depend on the treatment adopted. Similar results were obtained regarding the sample (A) also. The experimental methods employed are the same as those given in Part I.

The author's thanks are due to Prof. T. R. Seshadri for his interest in this work.

REFERENCES

1. P. B. R. Murti and T. R. Seshadri .. *Proc. Ind. Acad. Sci.*, 1940, **12**, 519.
2. K. Akagi .. *J. Cellulose Inst. Tokyo.*, 1939, **15**, 59–60.

SYNTHETICAL EXPERIMENTS IN THE GROUP OF SYMPATHOMIMETICS

Part II. Poly- and Hetero-cyclic Ring Systems

By S. Rajagopalan

(From the Department of Pure and Applied Chemistry, Indian Institute of Science, Bangalore)

Received March 24, 1941

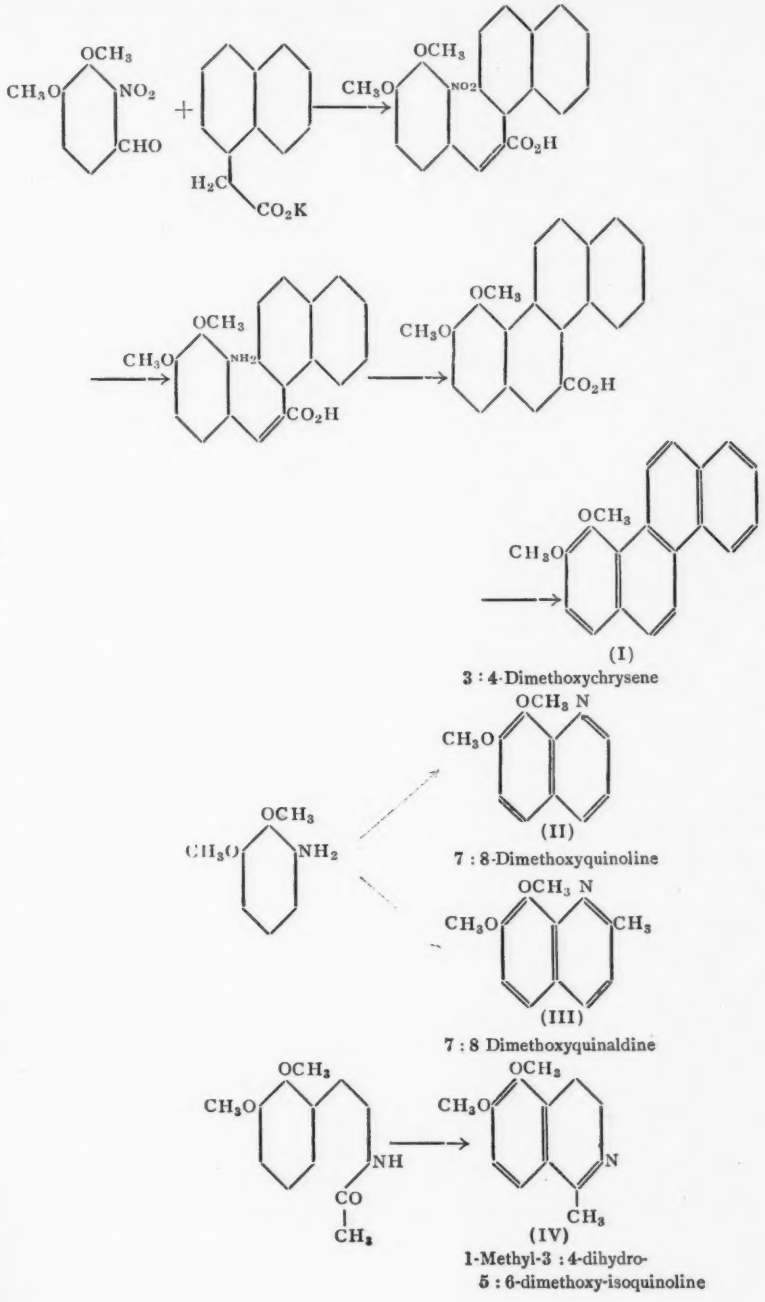
(Communicated by Prof. Sir C. V. Raman Kt., F.R.S., N.L.)

An earlier paper described the synthesis of some naphthalene compounds,[1] possessing the requisite structure necessary for sympathomimetic activity. In accordance with the programme of the study of the relation between chemical constitution and physiological activity, the present communication is concerned with attempts to synthesise a new group of sympathomimetically active amines in which the customary benzene nucleus of such substances was replaced by the phenanthrene, chrysene, quinoline and isoquinoline rings. In addition, the synthesis of a few more naphthalene compounds of this group was attempted incidentally.

It may be well to stress the fact that the scheme so far as it relates to the new ring-systems involves two distinct steps. First, the choice has to be made of starting materials containing the ring-systems with the requisite groups in suitable positions and without the β-amino ethyl side-chain. Secondly, the methods for the introduction of the aminoethyl chain in a favourable position in these substances have to be explored.

Actually, four (Nos. I–IV) of the starting materials (I–VI) chosen had to be synthesised for the first time for purposes of the present study, as under the first category. The additional naphthalene compounds that were included in the scheme were α-naphthol and 1 : 2-dihydroxy naphthalene.

The classical method of Pschorr as modified by Bogert and co-workers[2] was adopted for the synthesis of 3 : 4-dimethoxy chrysene (I), starting from *o*-nitro-veratraldehyde[3] and α-naphthyl acetic acid.[4]



(I)
3 : 4-Dimethoxychrysene

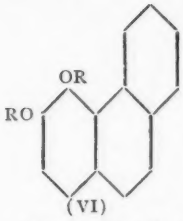
(II)
7 : 8-Dimethoxyquinoline

(III)
7 : 8 Dimethoxyquinaldine

(IV)
1-Methyl-3 : 4-dihydro-
5 : 6-dimethoxy-isoquinoline

(V)

8-Hydroxyquinoline



(VI)

Morphol (R=H); Morphol dimethyl ether ($R = CH_3$)

The dimethoxy quinoline (II) and the dimethoxy quinaldine (III) were prepared in good yields from *o*-amino-veratrole[5] by application of the Skraup and the Doebner-Miller reactions respectively. The dimethoxy isoquinoline (IV) was obtained by cyclisation of the N-acetyl derivative of 2: 3-dimethoxy phenylethylamine[6] by means of the usual Bischler-Napieralsky procedure.

In order to carry out the second stage of the scheme, it was decided, in the first instance, to examine the applicability to the present case of an apparently direct and elegant method, developed by Hinsberg,[7] consisting in the smooth condensation of phenols and phenol ethers with amino acetal. The reaction, which was studied under a variety of conditions, was successful so far as α-naphthol was concerned, but gave rise to by-products or did not proceed at all in the case of others. α-Naphthol gave in good yields a hydrochloride, $(HO \cdot C_{10}H_6)_2 CH \cdot CH_2NH_2, HCl$. The products obtained from 1: 2-dihydroxy naphthalene and 3: 4-dihydroxy phenanthrene (VI, R = H) were characteristically unstable and non-crystalline and only in the case of the latter was it possible to prepare a stable picrate. The attempts with 8-hydroxy-quinoline (V) proved fruitless, the original compound being recovered unreacted. The condensation of the dimethoxy heterocyclics (II, III, IV) with aminoacetal was expected to yield products having an ethanol amine chain, $R \cdot CH(OH) \cdot CH_2 \cdot NH_2$, which could then be demethylated to give analogues of 'arterenol'. This expectation has, however, not been realised, the dimethoxy hetero-cyclics like 8-hydroxyquinoline being unreactive.

The Friedel-Craft reaction between morphol dimethyl ether (VI, R = CH_3) and hippuryl chloride gave 3: 4-dimethoxy-N-benzoyl-ω-aminoacetophenanthrone, but, however, in poor yields. Hence the use of the material for the ultimate synthesis of 3: 4-dihydroxy phenanthryl ethanolamine could not be contemplated.

It is hoped to make further trials to condense aminoacetal with the various compounds described above changing, necessarily, the experimental

conditions. It is also proposed to investigate other methods for the introduction of the β-aminoethyl side-chain in these ring-systems. These studies will form the subject of a further communication.

Experimental

Synthesis of 3 : 4-*dimethoxychrysene* (I):

α-*Naphthyl*-2-*nitro*-3 : 4-*dimethoxycinnamic acid.*—A mixture of potassium α-naphthyl acetate (44. g.), 2-nitroveratraldehyde (39·5 g.) and freshly distilled acetic anhydride (275 c.c.) was heated in an oil-bath at 105–10° for 24 hours, cooled and the excess of acetic anhydride cautiously decomposed with water. The resulting acrylic acid was purified through an ammoniacal solution and crystallised from alcohol as yellow needles, m.p. 238–39° (decomp.); yield 56 g. (Found: C, 66·31; H, 4·39. $C_{21}H_{17}O_6N$ requires C, 66·49; H, 4·49 per cent.)

α-*Naphthyl*-2-*amino*-3 : 4-*dimethoxy-cinnamic acid.*—A mixture of ferrous sulphate hexahydrate (303 g.), liquor ammonia (70 c.c.) and water (1 litre) was boiled and treated with a mixture of the nitro-acid (55 g.) and concentrated ammonia. Ammonia (550 c.c.) was then added in the course of the next half hour, followed by more (150 c.c.) during a further 45 minutes. The reaction mixture was filtered hot, and the residue washed thrice with hot dilute ammonia. The amino-acid was liberated by addition of acetic acid and crystallised from alcohol as almost colourless, prismatic needles, m.p. 201° (decomp.); yield 35 g. (Found: C, 71·72; H, 5·10. $C_{21}H_{19}O_4N$ requires C, 72·21; H, 5·45 per cent.)

3 : 4-*Dimethoxy-chrysene*-11-*carboxylic acid.*—The crude amino-acid (32 g.) suspended in *iso*amyl ether (200 c.c.) was treated with concentrated sulphuric acid (4·9 c.c.) followed by freshly prepared *iso*amyl nitrite (12·2 c.c.), and the mixture shaken for 3 hours when it almost solidified. It was then added to a solution of sodium hypophosphite (70 g.) in water (70 c.c.) containing a little active copper at 40–50°, heated upto 80° and kept at 80–90° with stirring for 1 hour, poured into excess of ammonia (2 liters), filtered and the aqueous solution acidified with hydrochloric acid. The crude acid (20 g.) was recrystallised from acetone, benzene-petroleum ether and finally alcohol as colourless needles, m.p. 200–02° (decomp.). (Found: C, 71·55; H, 5·05. $C_{21}H_{16}O_4H_2O$ requires C, 71·99; H, 5·15 per cent.)

3 : 4-*Dimethoxychrysene* (I).—The above crude acid (5 g.) was refluxed with quinoline (30 c.c.) and a little copper powder for 1½ hours and worked up in the usual way for a neutral substance. The dimethoxy chrysene was obtained as a pale, viscous oil, b.p. 210–20°/ 1–2 mm.; yield 3·2 g. (Found: C, 82·74; H, 5·38. $C_{20}H_{16}O_2$ requires C, 83·83; H, 5·56 per cent.)

The *picrate* crystallised from alcohol as yellow needles, m.p. 153–55° (decomp.). (Found: C, 58·19; H, 4·17. $C_{26}H_{19}O_9N_3 \cdot H_2O$ requires C, 58·33; H, 3·92 per cent.)

7 : 8-*Dimethoxyquinoline* (*II*).—Glycerine (36·7 g.), nitrobenzene (6·7 g.) concentrated sulphuric acid (26·7 g.) and *o*-amino-veratrole (12 g.) were heated together on the water-bath for 1 hour, transferred to a metal-bath at 100° and the temperature gradually raised to 135°, when a violent reaction set in. The flask was removed and after violence had subsided was heated at 130–35° for 3 hours. The mixture was poured into water, extracted thrice with ether, the aqueous layer cooled, basified with excess of dilute sodium hydroxide and extracted thoroughly with ether. The extract was washed, dried over anhydrous sodium carbonate and the solvent distilled off. The residual oil was heated with acetic anhydride (10 c.c.) and a little sodium acetate on the water-bath for 2 hours, poured into water and extracted with ether. The aqueous solution was cooled, basified with excess of sodium hydroxide and repeatedly extracted with ether. The ether extract was washed, dried and distilled. The dimethoxyquinoline was a faintly yellow oil b.p. 148–50°/3 – 4 mm.; yield 8·5 g. (Found: C, 69·20; H, 5·52. $C_{11}H_{11}O_2N$ requires C, 69·84; H, 5·82 per cent.)

The *picrate* crystallised from alcohol in yellow needles, m.p. 182–84° after softening at 180°. (Found: N, 13·39. $C_{17}H_{14}O_9N_4$ requires N, 13·40 per cent.)

The *methiodide* crystallised from chloroform-benzene in yellow needles, m.p. 182° (decomp.) Found: I, 37·86. $C_{12}H_{14}O_2NI$ requires I, 38·37 per cent.)

7 : 8-*Dimethoxyquinaldine* (*III*).—A mixture of *o*-amino-veratrole (15·3 g.), concentrated hydrochloric acid (35 c.c.) and zinc chloride (6 g.) was cooled, treated with freshly distilled paraldehyde (20 g.) and heated on the boiling water-bath for 1½ hours, transferred to a metal-bath at 100°, and the temperature gradually raised to 130° and refluxed at 130–35° for 4 hours, cooled and poured into water and worked up in the same way as for the quinoline derivative (II). The quinaldine was obtained as a thick yellow oil, b.p. 147–48°/2–3 mm.; yield 7·5 g. (Found: C, 71·23; H, 6·12. $C_{12}H_{13}O_2N$ requires C, 70·94; H, 6·40 per cent.)

The *picrate* separated from alcohol in yellow needles, m.p. 155–56° (decomp.). (Found: N, 11·88. $C_{18}H_{16}O_9N_4$ requires N, 12·96 per cent.)

The *methiodide* crystallised from chloroform containing a trace of methanol in yellow needles, m.p. 176–77° (decomp.). (Found: I, 35·99. $C_{13}H_{16}O_2NI$ requires I, 36·81 per cent.)

1-*Methyl*-3 : 4-*dihydro*-5 : 6-*dimethoxy isoquinoline* (*IV*) *and Its Derivatives*:

β-(2 : 3-*Dimethoxy*)-*phenylethyl acetamide*, prepared in the usual way, separated from benzene-petroleum ether in long, colourless needles, m.p. 64–66°. (Found: N, 6·24. $C_{12}H_{17}O_3N$ requires N, 6·28 per cent.)

The *dihydroisoquinoline* (*IV*).—A mixture of the above amide (crude m.p. 61–3°; 11·4 g.) in dry toluene (75 c.c.) and phosphorus oxychloride (30 c.c.) was gently refluxed on the sand-bath for 2 hours with the exclusion of moisture, cooled and poured on to crushed ice. The aqueous solution was extracted with ether, cooled, basified with excess of ammonia and repeatedly extracted with ether. The extract was washed, dried over anhydrous sodium carbonate and distilled. The *iso*quinoline was a faintly yellowish oil, b.p. 141–43°/3 mm.; yield 8·5 g. (Found: C, 70·11; H, 7·14. $C_{12}H_{15}O_2N$ requires C, 70·25; H, 7·32 per cent.)

The *hydrochloride* crystallised from alcohol-ether in colourless needles, m.p. 202-03° (decomp.). (Found: Cl, 14·6. $C_{12}H_{16}O_2NCl$ requires Cl, 14·16 per cent.)

The *picrate* separated from alcohol-acetic acid in yellow needles, m.p. 214° (decomp.) after slight sintering at 210°. (Found: N, 12·67. $C_{18}H_{18}O_9N_4$ requires N, 12·90 per cent.)

The *methiodide* crystallised from chloroform-benzene in colourless, silky needles, m.p. 106–07° (decomp.). (Found: I, 36·48. $C_{13}H_{18}O_2NI$ requires I, 36·60 per cent.)

1-*Methyl*-5 : 6-*dimethoxy*-1 : 2 : 3 : 4-*tetrahydroisoquinoline*.—The dihydro base (1 g.) in sulphuric acid (40 c.c. of 1 : 3) was heated with zinc dust (5 g.) on the boiling water-bath for 4 hours. The solution was cooled, basified with a large excess of ammonia and extracted with ether. The extract after washing, drying and distilling gave the tetrahydro-*iso*quinoline as a pale yellow oil; yield 1 g.

The *hydrochloride* separated from alcohol-ether in colourless needles, m.p. 213–14° (decomp.). (Found: Cl, 14·13. $C_{12}H_{18}O_2NCl$ requires Cl, 14·05 per cent.)

The *picrate* separated from alcohol in yellow, prismatic needles, m.p. 196–98° (decomp.), after sintering at 194°. (Found: N, 12·82. $C_{18}H_{20}O_9N_4$ requires N, 12·84 per cent.)

β, β-Bis (4-*hydroxy-naphthyl*)-*ethylamine hydrochloride*.—A mixture of *α*-naphthol (2·1 g.), aminoacetal (1 g.) and glacial acetic acid (8 c.c.) was treated with concentrated hydrochloric acid (15 c.c.), allowed to stand at room temperature for 3 days and treated with hydrochloric acid till complete separation of the hydrochloride. The separated crystals were filtered,

washed with a little acetic acid followed by alcohol-ether and recrystallised from alcohol-ether as white, feathery needles, m.p. 237–38° (decomp.); yield 1·4 g. (Found: Cl, 9·20. $C_{22}H_{20}O_2NCl$ requires Cl, 9·47 per cent.)

β-(3 : 4-*Dihydroxy*-) *phenanthryl-β-hydroxy-ethylamine.*—A mixture of morphol (1·8 g.), aminoacetal (1·3 g.), acetic acid (12 c.c.) and concentrated hydrochloric acid (23 c.c.) was allowed to stand at room temperature for 3 days, poured into excess of water and filtered from considerable amount of tarry matter. The aqueous solution, after freeing from non-basic impurities by extraction with ether, was evaporated under reduced pressure. An aqueous solution of the residue on treatment with Hager's reagent gave the *picrate* as a greenish yellow powder, after washing repeatedly with alcohol and acetic acid, decomposing at 195–97°. (Found: N, 10·74. $C_{22}H_{18}O_{10}N_4$ requires N, 11·24 per cent.)

3 : 4-*Dimethoxy-N-benzoyl-ω-aminoacetophenanthrone.*—3 : 4-Dimethoxy-phenanthrene (VI, R = CH_3; 6 g.) in carbon bisulphide (50 c.c.) was condensed with hippuryl chloride (7 g.) in the presence of anhydrous aluminium chloride (7 g.) and worked up in the usual way. The reaction product was obtained as a thick oil which solidified in contact with alcohol-acetic acid. The ketone crystallised from acetic acid as almost colourless plates, m.p. 268–69° (decomp.). (Found: C, 74·82; H, 5·18. $C_{25}H_{21}O_4N$ requires, C, 75·18; H, 5·51 per cent.)

Summary

With a view to study the relation between chemical constitution and physiological activity, attempts have been made chiefly to synthesise a group of sympathomimetically active amines derived from phenanthrene, chrysene, quinoline and *iso*quinoline ring-systems.

3 : 4-Dimethoxy chrysene, 7 : 8-dimethoxy-quinoline, 7 : 8-dimethoxy quinaldine and 1-methyl-3 : 4-dihydro-5 : 6-dimethoxy-*iso*quinoline, which were required as intermediates, have been synthesised.

The author's grateful thanks are due to Prof. P. C. Guha for his interest in the work and to the Government of Madras for the award of a scholarship.

REFERENCES

1. Rajagopalan .. *J. Ind. Chem. Soc.*, 1940, **17**, 567.
2. Bogert and co-workers .. *J. Amer. Chem. Soc.*, 1939, **61**, 2463, 3055.
3. Slotta and Lauerson .. *J. prakt. Chem.*, 1934, **139**, 220.
4. Combron .. *Canad. J. Research.*, 1939, **17**, 10;
   Manske and Leddingham .. *Ibid.*, 1939, **17**, 14.
5. Mauthner .. *J. prakt. Chem.*, 1937, **149**, 328.
6. Haworth .. *J. Chem. Soc.*, 1927, 2281.
7. Hinsberg .. *Ber.*, 1923, **56**, 852.

483-41.—Printed at The Bangalore Press, Bangalore City, by G. Srinivasa Rao, Superintendent and Published by The Indian Academy of Sciences, Bangalore

ERRATA

Vol. XIII, No. 5, May 1941

Page 345: *Omit* the power $\frac{1}{2}$ on the R.H.S. of equation (27).

Page 349: In the equation for ρ_1 in (54) *replace* $(\delta_1 + 3\,\delta_0\,\theta)$ *by* $(\delta_1 - 3\,\delta_0\,\theta)$.

INDEX TO VOL. XIII (A)

AUTHORS' INDEX

Ali, S. Ashroff, Desai, R. D., and Shroff, H. P.	Heterocyclic compounds, Part XIII, 184.
Ananthakrishnan, S. V., and Pasupati, V.	Substitution in polycyclic systems. Part II, 211.
Bajpai, R. R., and Vaidhianathan, V. I.	On the preparation of quartz ultrasonic oscillators, 504.
Balakrishnan, T. A. S. ..	An elementary theory of the coronas of water-droplets, 188.
Barve, P. M. ..	*See* Vora and others.
Bhabha, H. J. ..	Note on the correspondence between the classical and quantum theories of neutral mesons, 249.
Bhabha, H. J., and Rao, B. S. Madhava	The scattering of charged mesons, 9.
Bhagavantam, S. ..	Raman effect in relation to crystal structure: Lattice oscillations, 543.
Bhagavantam, S., and Bhimasenachar, J.	Modified reflection of X-rays: Naphthalene, 266.
Bhat, R. V. ..	Adaptation of the Micro-Kjeldahl method to the estimation of nitrogen in organic compounds containing nitro and azo groups, 269.
Bhimasenachar, J. ..	*See* Bhagavantam and Bhimasenachar.
Bokil, K. V., and Nargund, K. S.	Syntheses in the chaulmoogric acid series, Part III, 233.
Chalam, E. V. ..	*See* Nath and Chalam.
Chiplonkar, V. T. ..	Rectification in discharge tubes—Part II, 323.
Deliwala, C. V., and Shah, N. M.	Aluminium chloride, a new reagent for the condensation of β-ketonic esters with phenols. Part V, 352.
Desai, B. N. ..	*See* Vora and others.
Desai, R. D. ..	*See* Ali and others.
Desai, R. D., and Hamid, Abdul	Studies in naphthalene series. VIII, IX, 126, 132.
Desai, R. D., and Waravdekar, W. S.	Studies in naphthalene series. Part VII, 39.
	Heterocyclic compounds. Part XII, 177.
Desai, R. D., Hamid, Abdul, and Shroff, H. P.	Studies in naphthalene series. Part VI, 33.
Deshpande, J. S. ..	*See* Hirwe and Deshpande.
Dharam Das, Ione Nitravati, and Tewari, J. D.	The effect of unsaturated chromophores on pyronine dyestuffs. Part II, 68.

Dharmatti, S. S. ..	Magnetism and molecular structure of sulphur compounds, 359.
Dixit, K. R. ..	Effect of admixture of silver on the rectifying properties of Cu-Cu_2O cells, 498.
Ganapathi, K. ..	Chemotherapy of bacterial infections. Part IV, 386.
Gavankar, (Miss) K. D.	*See* Hirwe and others.
Gupta, Hansraj ..	An important congruence, 85.
	Some idiosyncratic numbers of Ramanujan, 519.
Hamid, Abdul ..	*See* Desai and Hamid.
	See Desai and others.
Hirwe, N. W., and Deshpande, J. S.	Studies in chloral amides. Part VIII, 275; Part IX, 277.
Hirwe, N. W., and Kulkarni, P. Y.	Studies in chloral amides—Part VII, 49.
Hirwe, N. W., and Patil, B. V.	Studies in chloral amides. Part VII, 273.
Hirwe, N. W., Gavankar, (Miss) K. D., and Patil, B. V.	Studies in chloral amides. Part X, 371.
Iyer, K. S. Sankarasubba	*See* Rao and Iyer.
Ittyerah, P. I., and Pandya, K. C.	Condensation of malonanilic acid with aldehydes. Part II, 119; Part II, 122; Part IV, 461.
Joglekar, S. Y. ..	*See* Ramdas and Joglekar.
Krishnan, K. G. ..	Dispersion of ultrasonic velocity in organic liquids, 281.
Krishnaswamy, B., and Seshadri, T. R.	Synthetic experiments in the benzo-pyrone series. Part III, 43.
Kulkarni, P. Y. ..	*See* Hirwe and Kulkarni.
Murti, P. Bhaskara Rama	A study of the chemical components of the roots of *Decalepis Hamiltonii* (makali veru). Part II, 263.
	Paper pulp from annual crops. Part II, 564.
Murti, P. Bhaskara Rama, and Seshadri, T. R.	A study of the chemical components of the roots of *Decalepis Hamiltonii* (makali veru). Part I, 221; Part II, 399.
	The glycosidic components of the flowers of *Butea frondosa*, 395.
Murty, G. V. L. N. ..	Ferric chloride as a permanent standard in the colourimetric estimation of nitrate, 116.
Narayanamurti, D., and Ranganathan, V.	The thermal conductivity of Indian timbers. Part I, 300.
Nargund, K. S. ..	*See* Bokil and Nargund.
Narlikar, V. V. ..	A classical limit of heavy homogeneous spherical masses, 240.
Nath, N. S. Nagendra, and Chalam, E. V.	The intensities of the Raman lines in carbon dioxide, 339.

Nayar, P. G. N. ..	Temperature variation of the Raman frequency of diamond, 284.
	Luminescence, absorption and scattering of light in diamonds: Part I, 483; Part II, 534.
Nedungadi, T. M. K. ..	Effect of crystal orientation on the Raman effect in naphthalene and benzophenone, 161.
Neelakantam, K. ..	Determination of lead permanganometrically (Low's method), 108.
Neelakantam, K., and Row, L. Ramachandra	The lanthanum nitrate test for acetate in inorganic qualitative analysis, 194.
Norris, R. ..	The Raman spectrum and the specific heat of crystalline sulphur, 291.
Pandya, K. C. ..	*See* Ittyerah and Pandya.
Paramasivan, S. ..	Electrolytic restoration of bronze statues and inscribed copper plates, 53.
	Investigations on ancient Indian metallurgy. I, 87.
Pasupati, V. ..	*See* Ananthakrishnan and Pasupati.
Patil, B. V. ..	*See* Hirwe and others.
	See Hirwe and Patil.
Pillai, S. S. ..	On the sum function connected with primitive roots, 526.
	On M consecutive integers—III, 530.
Rajagopalan, S. ..	Synthetical experiments in the group of sympathomimetics. Part II, 566.
Raman, C. V. ..	Crystals and photons, 1.
Ramdas, L. A., and Joglekar, S. Y.	Studies on thermal repulsion, 374.
Ram, Gurdas, and Vaidhianathan, V. I.	On capillary forces in natural soils, 77.
Ranganathan, V. ..	*See* Narayanamurti and Ranganathan.
Rangaswami, S., Seshadri, T. R., and Venkateswarlu, V.	The remarkable fluorescence of certain coumarin derivatives, 316.
Rao, B. S. Madhava ..	*See* Bhabha and Rao.
Rao, D. A. A. S. Narayana	Raman effect in gypsum, 137.
Rao, K. Ranganatha, and Seshadri, T. R.	Synthesis of 7-hydroxy-5-methylcoumarin, 255.
Rao, S. Ramachandra, and Iyer, K. S. Sankarasubba	Photoelectric efficiency of ferromagnetic metals at different temperatures in the soft X-ray region, 411.
Rao, V. Subba, and Seshadri, T. R.	Chemical investigation of Indian lichens. Part III, 199.
Row, L. Ramachandra ..	*See* Neelakantam and Row.
Row, L. Ramachandra, and Seshadri, T. R.	Pyrilium salts derived from 4-O-methyl resorcylic aldehyde, 510.

Saksena, B. D. .. Raman spectrum of gypsum, 25.

Sarkar, T. C. .. The lead ratio of a crystal of monazite from the Gaya District, Bihar, 245.

Seshadri, T. R. .. *See* Krishnaswamy and Seshadri.
See Murti and Seshadri.
See Rangaswami and others.
See Rao and Seshadri.
See Row and Seshadri.

Seshadri, T. R., and Venkateswarulu, V. Synthetic experiments in the benzopyrone series. Part IV, 404.

Seth, B. R. .. On the gravest mode of some vibrating systems, 390.

Seth, I. D. .. Reflection and refraction of attenuated waves in semi-infinite elastic solid media, 151.

Shabbar, Mohammad .. On the existence of a metric for path spaces admitting the Lorentz group, 203.

Shah, N. M. .. *See* Deliwala and Shah.

Shastri, N. A. .. Some relations between Bessel functions of third order and confluent hypergeometric functions, 521.

Shroff, H. P. .. *See* Desai and others.
See Ali and others.

Subrahmanian, R. V. .. The spectral character of reflection by a regularly stratified medium: Part I, 467.

Sunanda Bai, K. .. Depolarisation of light scattered by liquids, 439.

Tewari, J. D. .. *See* Dharam Dass and Tewari.

Vaidhianathan, V. I. .. *See* Ram and Vaidhianathan.
See Bajpai and Vaidhianathan.

Vaidyanathaswamy, R. .. The ideal-theory of partially ordered set, 94.

Venkataraman, R. .. The kinetics of the olefin-bromine reaction. Part III, 259.

Venkateswarlu, K. .. Relative intensities of Stokes and anti-Stokes Raman lines in crystals, 64.

Venkateswarlu, V. .. *See* Rangaswami and others.
See Seshadri and Venkateswarlu.

Vora, V. C., Barve, P. M., and Desai, B. N. Importance of dialysis in the study of colloids. Part VII, 100.

Waravdekar, W. S. .. *See* Desai and Waravdekar.

TITLE INDEX

Acetate in inorganic qualitative analysis, lanthanum nitrate test (Neelakantam and Row), 194.

Aluminium chloride, a new reagent for the condensation of β-ketonic esters with phenols, V (Deliwala and Shah), 352.

Benzo-pyrone series, synthetic experiments, III (Krishnaswamy and Seshadri), 43; IV (Seshadri and Venkateswarlu), 404.

Bessel functions of third order and confluent hypergeometric functions, some relations between (Shastri), 521.

Butea frondosa, flowers, the glycosidic components (Murti and Seshadri), 395.

Capillary forces in natural soils (Ram and Vaidhianathan), 77.

Chaulmoogric acid series, syntheses, III (Bokil and Nargund), 233.

Chemotherapy of bacterial infections, IV (Ganapathi), 386.

Chloral amides, studies, VII (Hirwe and Kulkarni), 49; VII (Hirwe and Patil), 273; VIII, IX (Hirwe and Deshpande), 275, 277; X (Hirwe and others), 371.

Chromophores, unsaturated, the effect, on pyronine dyestuffs, II (Dass and Tewari), 68.

Classical limit of heavy homogeneous spherical masses (Narlikar), 240.

Colourimetric estimation of nitrate, ferric chloride as a permanent standard (Murty), 116.

Congruence, important (Gupta), 85.

Coronas of water droplets, an elementary theory (Balakrishnan), 188.

Crystals and photons (Raman), 1.

Decalepis Hamiltonii (makali veru), roots, a study of the chemical components I, III (Murti and Seshadri), 221, 399; II (Murti), 263.

Depolarisation of light scattered by liquids (Sunanda Bai), 439.

Dialysis, importance, in the study of colloids, VII (Vora and others), 100.

Diamonds, luminescence, absorption, and scattering of light, I, II (Nayar), 483, 534.

Electrolytic restoration of bronze statues and inscribed copper plates (Paramasivan), 53.

Fluorescence, remarkable, of certain coumarin derivatives (Rangaswami and others), 316.

Gravest mode of some vibrating systems (Seth), 390.

Heterocyclic compounds, XII (Desai and Waravdekar), 177; XIII (Ali and others), 184.

Ideal-theory of the partially ordered set (Vaidyanathaswamy), 94.

Integers, M consecutive, III (Pillai), 530.

Kinetics of the olefin-bromine reaction, III (Venkataraman), 259.

Lead, determination, permanganometrically (Low's method) (Neelakantam), 108.

Lead ratio of a crystal of monazite from the Gaya District, Bihar (Sarkar), 245.

Lichens, Indian, chemical investigation, III (Rao and Seshadri), 199.

Magnetism and molecular structure of sulphur compounds (Dharmatti), 359.

Malonanilic acid, condensation, with aldehydes, II, III, IV (Ittyerah and Pandya), 119, 122, 461.
Mesons, charged, the scattering of (Bhabha and Rao), 9.
Mesons, neutral, note on the correspondence between the classical and quantum theories (Bhabha), 249.
Metallurgy, ancient Indian, investigations (Paramasivan), I, II, 87.
Metric, on the existence, for path spaces admitting the Lorentz group (Shabbar), 203.
Micro-Kjeldahl method, adaptation, to the estimation of nitrogen in organic compounds containing nitro and azo groups (Bhat), 269.
Naphthalene series, studies, VI (Desai and others), 33; VII (Desai and Waravdekar), 39; VIII, IX (Desai and Hamid), 126, 132.
Paper pulp from annual crops, II (Murti), 564.
Photoelectric efficiency of ferromagnetic metals at different temperatures in the soft X-ray region (Rao and Iyer), 411.
Polycyclic systems, substitution, II (Ananthakrishnan and Pasupati), 211.
Pyrilium salts derived from 4-O-methyl resorcylic aldehyde (Row and Seshadri), 510.
Quartz ultrasonic oscillators, on the preparation (Bajpai and Vaidhianathan), 504.
Raman effect in gypsum (Rao), 137.
Raman effect in naphthalene and benzophenone, effect of crystal orientation (Nedungadi), 161.
Raman effect in relation to crystal structure: Lattice oscillations (Bhagavantam), 543.
Raman frequency of diamond, temperature variation (Nayar), 284.
Raman lines in carbon dioxide, the intensities (Nath and Chalam), 339.
Raman lines in crystals, relative intensities of Stokes and anti-Stokes (Venkateswarlu), 64.
Raman spectrum and the specific heat of crystalline sulphur (Norris), 291.
Raman spectrum of gypsum (Saksena), 25.
Ramanujan, some idiosyncratic numbers (Gupta), 519.
Rectification in discharge tubes, II (Chiplonkar), 323.
Rectifying properties of Cu-Cu_2O cells, effect of admixture of silver (Dixit), 498.
Reflection by a regularly stratified medium, the spectral character, I (Subrahmanian), 467.
7-hydroxy-5-methyl coumarin, synthesis (Rao and Seshadri), 255.
Sum function connected with primitive roots (Pillai), 526.
Sympathomimetics, group, synthetical experiments, II (Rajagopalan), 566.
Thermal conductivity of Indian timbers, I (Narayanamurti and Ranganathan), 300.
Thermal repulsion, studies (Ramdas and Joglekar), 374.
Ultrasonic velocity, dispersion, in organic liquids (Krishnan), 281.
Waves, attenuated, reflection and refraction, in semi-infinite elastic solid media (Seth), 151.
X-rays, modified reflection: Naphthalene (Bhagavantam and Bhimasenachar), 266.

NOTICE TO AUTHORS

Scientific papers intended for publication in the *Proceedings of the Indian Academy of Sciences* can be accepted only when they are communicated by a Fellow of the Academy whose duty shall be to satisfy himself that such communications are fit to be read at the Meeting of the Academy and published in its *Proceedings*.

Papers should not ordinarily exceed fifty pages of foolscap. MSS. should be either typewritten or written in legible hand on one side of the paper. All papers should be carefully revised by the authors and should be absolutely in final form for printing. Position for text-figures should be indicated. Each paper shall conclude with a critical summary not exceeding 350 words.

Drawings, diagrams or other illustrations should be made on larger scale (preferably twice the size) than the ones in which they are intended to appear. They should be done in Indian ink on bristol board with lettering in pencil. Scale of magnification of camera lucida tracings should be indicated by the side of drawings. In certain special cases arrangements will also be made for monochrome lithographic and other colour plates. Reduction of illustrations desired should be indicated in pencil. Appropriate legends should accompany all drawings. Names of authors are to be marked in pencil on the left-hand corner of drawing sheets. Photomicrographs should be securely mounted with colourless paste.

All tables, quotations and footnotes which will be set hereafter (beginning from Vol. I, No. 2) in types smaller than the text, should be typewritten on separate sheets and placed with the text in proper sequence. Footnotes should be numbered in Arabic numerals.

References to literature in the text should be given, whenever possible, in chronological order, only the names of authors and years of publication, in brackets, being given. They should be cited in full after the summary, the authors' names following in alphabetical order. Thus,

Name or Names of authors; Name of Journal (abbreviation) with a single underline; Year of publication; Number of volume with a double underline, and lastly page. The following would be a useful illustration:—

Bergmann and Stather . . . . . Z. Physiol. Chem., 1926, 152, 189.

Two copies of slip-proof and wherever possible, a page proof for final revision will be sent to authors. All corrections are best made on the slip-proof which should be transmitted to the Office of the Academy. All proof corrections involve heavy expenses which would be negligible if the papers are carefully revised by the authors before submission.

Authors will be supplied with fifty copies of the contribution gratis and may buy additional copies at a small price if intimation is given at the time of returning the slip-proof.

All the blocks printed in the "Proceedings" will be offered to the respective authors at a price of 25% of the actual cost of preparing the blocks plus the packing and postal charges or railway freight to be incurred for despatching them, it being understood that authors should give due acknowledgment to the Academy whenever such blocks are reproduced in other journals.

The original drawings and plates of blocks appearing in the *Proceedings* will be returned to such of the authors as may require them provided the cost of despatching such originals is borne by them.

CONTENTS

The Spectral Character of the Reflection by a Regularly Stratified Medium : Part I . . . . . R. V. SUBRAHMANIAN 467

Luminescence, Absorption and Scattering of Light in Diamonds: Part I. Fluorescence. . . . . P. G. N. NAYAR 483

Effect of Admixture of Silver on the Rectifying Properties of Cu-Cu_2O Cells . . . . . K. R. DIXIT 498

On the Preparation of Quartz Ultrasonic Oscillators . . . . . R. R. BAJPAI AND V. I. VAIDHIANATHAN 504

Pyrilium Salts derived from 4-O-Methyl Resorcylic Aldehyde . . . . . L. RAMACHANDRA ROW AND T. R. SESHADRI 510

Some Idiosyncratic Numbers of Ramanujan . . HANSRAJ GUPTA 519

Some Relations between Bessel Functions of Third Order and Confluent Hypergeometric Functions . . . .N. A. SHASTRI 521

On the Sum Function Connected with Primitive Roots. S. S. PILLAI 526

On M Consecutive Integers—III . . . . . S. S. PILLAI 530

Luminescence, Absorption and Scattering of Light in Diamonds : Part II. Phosphorescence . . . . . P. G. N. NAYAR 534

Raman Effect in Relation to Crystal Structure: Lattice Oscillations . . . . . S. BHAGAVANTAM 543

Paper Pulp from Annual Crops. Part II. A Note on the Yields and Characteristics of Pulps from Different Vareities of Rice Straw . . . . . P BHASKARA RAMA MURTI 564

Synthetical Experiments in the Group of Sympathomimetics. Part II. Poly- and Hetero-cyclic Ring Systems. S. RAJAGOPALAN 566